**U.S. DEPARTMENT OF COMMERCE**
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PB-256 691

# Pollutant Potential of Raw & Chemically Fixed Hazardous Industrial Wastes and Flue Gas Desulfurization Sludges

**Army Engineer Waterways Experiment Station**

**Prepared For**
**Municipal Environmental Research Lab.**

July 1976

246141

PB 256 691

EPA-600/2-76-182
July 1976

Environmental Protection Technology Series

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

## TECHNICAL REPORT DATA

*(Please read Instructions on the reverse before completing)*

1. REPORT NO.
EPA-600/2-76-182

2.

3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE
POLLUTANT POTENTIAL OF RAW AND CHEMICALLY FIXED HAZARDOUS INDUSTRIAL WASTES AND FLUE GAS DESULFURIZATION SLUDGES - INTERIM REPORT

5. REPORT DATE
July 1976 (Issuing Date)

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Environmental Effects Laboratory
U.S. Army Engineer Waterways Experiment Station
Vicksburg, Mississippi 39180

10. PROGRAM ELEMENT NO.
1DC618 SOS #3/02
EHE624 COS

11. CONTRACT/GRANT NO.
IAG-D4-0569

12. SPONSORING AGENCY NAME AND ADDRESS
Municipal Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

13. TYPE OF REPORT AND PERIOD COVERED
Interim Jan. - Aug. 1975

14. SPONSORING AGENCY CODE
EPA-ORD

15. SUPPLEMENTARY NOTES
Robert E. Landreth, Project Officer 513/684-7871

16. ABSTRACT
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Major points of discussion within this report are the methods for physical and chemical analyses, documentation of the various sludge fixation processes, and a discussion of physical and chemical data that are presently available. Since the project is only partially completed, parameters and data have been selected that are representative of current progress. Physical data include the description parameters for the raw sludges and engineering properties of the fixed sludges that have been completed. Chemical properties related to leachate testing include the descriptive parameters pH and conductivity, plus the pollutants sulfate and copper.

17. KEY WORDS AND DOCUMENT ANALYSIS

| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
|---|---|---|
| Wastes, Stabilization, Leaching, Sludge, Ground Water, Permeability, Pollution, Sulfates, Sulfites | Leachate, Solid Waste Management, Flue Gas Cleaning, Chemical Stabilization (Fixation) | 13B |

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS (This Report)
UNCLASSIFIED

20. SECURITY CLASS (This page)
UNCLASSIFIED

21. NO. OF PAGES
117

22. PRICE

EPA Form 2220-1 (9-73)

☆USGPO: 1976 — 657-695/5468 Region 5-II

EPA-600/2-76-182
July 1976

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## Interim Report

by

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Interagency Agreement No. EPA-IAG-D4-0569

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# FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This research was supported by the EPA so that the Agency will have the required data base in the event guidelines become necessary for stabilization technology. This research will provide data to assist in making sound engineering decisions for the stabilization technology.

Francis T. Mayo
Director
Municipal Environmental
Research Laboratory

# ABSTRACT

This report presents an interim summary of current research dealing with the effects of chemical fixation on disposal of hazardous industrial waste residues and flue gas desulfurization (FGD) sludges. Present research involves both leaching and physical tests of raw and chemically fixed industrial wastes and FGD sludges. The intent of the study is to examine the potential environmental impact of raw sludge disposal and to assess the technical merits of sludge fixation as a disposal pretreatment process. Both objectives are being accomplished by leachate testing, which can be evaluated by comparison to the raw sludges and by durability testing, which reflects the environmental stability of the fixed products.

Major points of discussion within this report are the methods for physical and chemical analyses, documentation of the various sludge fixation processes, and a discussion of physical and chemical data that are presently available. Since the project is only partially completed, parameters and data have been selected that are representative of current progress. Physical data include the descriptive parameters for the raw sludges and engineering properties of the fixed sludges that have been completed. Chemical properties related to leachate testing include the descriptive parameters pH and conductivity, plus the pollutants sulfate and copper.

This report is submitted in partial fulfillment of Interagency Agreement Number EPA-IAG-D4-0569 between the U. S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Solid and Hazardous Waste Research Division (EPA, MERL, SHWRD) and the U. S. Army Waterways Experiment Station (WES). Work for this report was conducted during the period of January to August 1975.

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# NOTE

All measurements in EPA documents are to be expressed in metric units. In the report, however, implementing this practice adversely affects clarity. Conversion factors for non-metric units used in this document are therefore given as follows:

| British | Metric |
|---|---|
| 1 $ft^2$ | 0.0929 $meters^2$ |
| 1 $ft^3$ | 0.0283 $meters^3$ |
| 1 $ft^3$/min | 28.316 l/min |
| 1 gpm | 3.785 l/min |
| 1 lb | 0.454 kg |
| 1 ton (short) | 0.9072 metric tons |

# ACKNOWLEDGMENTS

The assistance of the firms and companies which provided samples of residues and performed fixation and these samples is gratefully acknowledged. Without the continued support of these companies, research projects of this nature could not be successfully performed.

The guidance and support of Mr. Robert E. Landreth and the Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, U. S. Environmental Protection Agency is greatly appreciated.

This project was conducted at the U. S. Army Engineer Waterways Experiment Station (WES) under the general supervision of Dr. John Harrison, Chief, Environmental Effects Laboratory (EEL), and Mr. Andrew J. Green, Chief, Environmental Engineering Division. The Soils and Pavements Laboratory (S&PL) provided physical property analyses under the direction of Mr. G. P. Hale; and the EEL Analytical Laboratory Groups, under the direction of Mr. J. D. Westhoff and Dr. D. W. Rathburn, provided guidance in selection of chemical testing procedures as well as chemical analysis of the sludges and leachates used. Technical support in maintaining and sampling the leaching facilities was provided by Messrs. Oscar W. Thomas, Johnnie E. Lee, and Jack H. Dildine.

Director of WES during the course of this study was Col. G. H. Hilt, CE. Technical Director was Mr. F. R. Brown.

# SECTION I

# INTRODUCTION

## BACKGROUND

The promulgation of air and water pollution control legislation has brought about an increase in the efficiency of equipment designed to remove pollutants from air and water discharge streams. The end product of treatment is usually a solid material, i.e., sludge or residue, that contains the removed pollutants in a concentrated form. (The terms residue and sludge will be used synonymously throughout this report.) Until recently, the disposal of sludge or residue was not considered an integral phase of the air or wastewater treatment processes. The realization that improper disposal of these residues may result in an adverse environmental impact[1] has reinforced the concept that proper environmental management and control must address all aspects of the environment -- air, water, and land. Since many residues contain pollutants in high concentrations, they may be referred to as hazardous because of the precautions required for disposal or handling.

The disposal of hazardous residues may be accomplished in several fashions. Incineration is useful as a volume reduction process and for complete destruction of synthetic compounds such as pesticides. Ocean disposal is practiced where it is feasible and where the environmental impact may be demonstrated to be small or none. Recovery and reuse of materials from residues is practiced when technology is available and there is an economic incentive. This latter concept is not a disposal operation, per se, but may be equated to a disposal operation by virtue of eliminating or reducing its need. Other promising treatment and/or disposal processes for hazardous wastes have been summarized recently.[2] Generally, the main receptor for most residues is the land through a landfill process, or similar disposal operations such as ponding or abandoned mine filling.

The practice of land disposal of residues is aimed at eventually returning all pollutants or materials to the environment. In the case of hazardous residues, the rate of pollutant migration from the disposal site to the surrounding air, land, or water may exceed that which is considered environmentally safe. Unsafe conditions may arise because of the pollutant concentration and its associated mobility for a particular residue, or through physical, chemical, or biological interaction of the residues with the surrounding environment. When land disposal of residues results in adverse environmental impact, further treatment of the residue may be required.

The principal method of treatment is creation of a barrier between the disposal site and the surrounding environment by use of a liner, or fixation of the residue. The use of liners is a feasible alternative and is justifiable when economics are favorable. Possible problems associated with the use of liners are unfavorable reactions with the residue (which may cause deterioration) or improper placement (which results in spot leaks). Fixation is defined as a process that retards the migration of pollutants from residues to the surrounding environment. As it is currently applied, fixation may be considered as the addition of materials that react with the residues or as an encapsulation process. Encapsulation is very similar to the use of liners in that a physical barrier is provided against pollutant mobility. In the use of admixing materials with the residues, either organic or inorganic materials may be used. In this mode, fixation generally reduces pollutant mobility through alteration of the chemical and physical properties of the residue. The chemical alterations are quite complex and are difficult to explain theoretically; however, the physical alterations generally take place by decreasing the surface-area-to-volume ratio by formation of a solidified mass. This latter alteration is advantageous in retarding pollutant migration through mass transport phenomena. The use of fixation is particularly desirable in the case of hazardous wastes, where it assures an environmentally proper disposal. The use of fixation for treatment also has its associated problems. Since fixation generally depends on a reaction of additives with the residues, it must be tested in advance to determine whether the desired reaction will take place and the proper conditions for reactions (viz. mixing, ratio or reagents, etc.). Additionally, the rate of leaching of pollutants from fixed materials may not be determined in advance and must be established by testing. Testing should consider all possible physical, chemical, and biological properties that may affect fixed material performance. Furthermore, testing should be performed over a sufficient time frame to allow prediction of future performance for the life of the disposal system. Realistically, it is not possible to test all system permutations, but testing should be sufficiently detailed to place confidence on the reliability of fixation in the field. The physical durability of the fixed material should be determined. Since alteration of residue geometry, or physical state, may be a chief advantage of fixation, adherence to those properties under handling or disposal conditions should be evaluated.

Since additional treatment of residues before disposal represents an added cost for overall treatment, the economics of fixation processes must also be considered. If economics are to be considered, they must be defined for each fixation process and in turn related to the potential application of that process. Generally, the economics may be represented as a tradeoff between costs and the degree of hazard associated with a particular residue. The degree of hazard is directly related to the environmental risk associated with the disposal operation process for a particular residue. Obviously, the higher the hazard and its risk for disposal, the higher the cost that may be associated with treatment.

## PURPOSE AND OBJECTIVES

The U. S. Army Waterways Experiment Station (WES) has undertaken, through an interagency agreement with the U. S. Environmental Protection Agency, a study directed at examining the potential utility of fixation processes for application to various sludges to yield products environmentally acceptable for disposal. The various sludge categories identified within the scope of work are residues associated with industrial processes and with flue gas desulfurization (FGD) systems. The specific objectives of the study are as follows:

(a) To assess on a laboratory scale the pollution potential, leachability, and physical durability of selected hazardous industrial residues, FGD residues, and fixed materials from these categories.

(b) To verify the laboratory data by field studies.

To accomplish these objectives, the study has been divided into three distinct phases: (1) residue characterization and experimental design, (2) laboratory testing, and (3) field testing. The first phase of the study was to serve as background for the remaining phases. This phase is complete and has been summarized in an earlier project report.[3] Phasing of the project has been designed to build a sufficient data base on which to base the evaluation of fixation technology. The pollutant potential of raw sludges has been included for comparative purposes since it represents an integral part of this study.

## SCOPE OF THIS REPORT

The purpose of this report is to summarize the project results from the last interim report.[3] A majority of this report summarizes fixation of the residue samples by the processors included in the laboratory program. Since the purpose of the study is to assess fixation technology, neither the participating processors nor the sources of sludges will be identified in this report. The remainder of the report will discuss current progress in physical testing and leach column testing. The data are limited since the laboratory program is not complete; consequently, those data presented are only a portion of the results deemed representative of the project. Since these data were limited at the time of this report, definite conclusions should not be made from the data presented here until all data is available.

Determination of process economics for fixation is not possible at this point in time, but the subject will be addressed in the subsequent project reports. Assessing the economics of several fixation processes for comparative purposes is difficult because of a number of factors. First, it is extremely difficult to obtain comparable cost data for a specific residue category. Second, many fixation processes are offered as services and capital costs are included in the service cost and not considered separately. Third, possible productive uses exist for some fixed residues that would offset processing costs.

# SECTION II
# SUMMARY

The purpose of this report is to summarize the project results from the last interim report.[3] The data are limited since the laboratory program is not complete; consequently, those data presented are only a portion of the initial nine month results deemed representative of the project.

Fixation of residues is characterized by alterations in geometry (surface area:volume) and changes in chemical environment. Retarding the leaching of pollutants by chemical fixation is process-dependent, but appears to be successful (although leaching rates for copper and sulfate are high for some residues and would probably exhibit an environmental impact). Leaching behavior for most samples can be related to a diffusion and/or solubility mechanism and appear to stabilize in time.

Leaching of copper from both raw and fixed residues was demonstrated for a majority of the samples tested. In most cases, initial leaching was above background levels (10 μg/ℓ), and some fixation processes were not successful in retarding the leaching of copper.

Leachate data for most specimens exhibited high initial concentrations of sulfate (> 1,000 mg/ℓ), followed by a gradual decrease. The leaching of sulfates is apparently related to solubility, which depends on the compounds present in specific specimens, particularly the FGD sludges. Fixation demonstrated an ability to retard sulfate leaching, but concentrations were high for certain samples.

Conductivities for leachates were strongly dependent on the type of residue, but observation of high leachate conductivities for most specimens seemed to indicate leaching of dissolved solids.

In fixed residues, pH seemed to be dependent on fixation additives, time, and volume of leaching solution applied. Convergence of leachate pH for raw and fixed sludges as a function of time appears to demonstrate that stability of the fixed sludges is a function of the volume of leaching solution applied. The pH of the leachate (for residue 100) was independent of the type of leaching solution applied, suggesting that pH was mainly dependent on the type of residue.

Raw sludges are physically characterized to be fine-grained materials of low density (40-60 PCF), similar in texture to silt and silt-loam. On this basis, low shear strength (2-8 PSI) and permeability ($< 10^{-4}$ cm/sec) are to be expected, although no laboratory testing was conducted for verification.

Fixation of sludges results in physical alterations that produce a hardened mass or a soil-like material characterized by increased dry densities (1-81% increase) and strength; fixed sludge characteristics are strongly dependent on the fixation process and type of sludge.

# SECTION III

# METHODS AND MATERIALS

## LEACHING TEST FACILITY

As mentioned previously, the primary concern in ultimate disposal of sludges is the rate of pollutant migration to the environment. To effectively determine the rate of pollutant migration, a leaching test has been devised. This leaching test is aimed at measuring the rate of pollutant movement. into an aqueous medium, and has been designed to represent field conditions as closely as possible. Details of this leaching test system have been previously documented,[3] and will only be summarized for this report. The principle factors to be considered in constructing a leaching facility include materials for construction of the system; specifications for sample preparation; and procedures for performing the leaching tests.

The specifications of material for construction are required to assure that the equipment may be considered inert with respect to the leach specimen and leachate. Since adequate information was not available regarding pollutant interaction with materials in this study, high grade plastics were selected for construction materials. To provide further assurances, adequate measures were taken to clean all materials and to establish controls for detection of any interactions.

The leaching columns are four inches inside diameter (I.D.) and constructed to contain a sample volume of approximately 0.35 cubic feet. The inlet port was placed approximately 1 inch above the top of the sample to maintain a fluid head of that height on the top of the sample. The columns were capped to minimize air contamination. The bottom of the column is constructed to collect the leachate through an outlet port. Flow through the columns is regulated by a stopcock to maintain a fluid velocity of approximately $1 \times 10^{-5}$cm/sec. This velocity corresponds to the permability through a very fine sand. A 3-inch layer of polypropylene pellets was placed in the bottom of each column to retard movement of suspended solids from the columns. This technique was used since field conditions will normally provide similar filtration capacity at the boundary of the sludge. Some of the fixed sludges assumed a definite physical shape and demonstrated structural rigidity. These samples were molded into 3-inch diameter forms, placed in the columns, and the annular ring filled with polypropylene pellets. This procedure created a dispersed flow around the columns, similar to field conditions. For all leaching tests, the specimens are maintained in a saturated flow condition.

Sample collection was made in 1-gallon polypropylene containers sealed with parafilm.

Two leaching fluids were used, deionized water saturated with carbon dioxide, pH 4.5 to 5.0, and deionized water buffered with boric acid, pH 7.5 to 8.0. Boric acid was selected since it is relatively inert and was used in a low concentration as not to effect the leaching properties of the samples. The two leaching fluids represent both sides of the pH scale and should provide some concept of the pH effect on leaching. Each set of columns was fed from a constant head reservoir. Sample columns were triplicated for each leaching solution and all columns were randomly assigned within the test system. All materials for the leach fluid distribution system were polypropylene or teflon to minimize exchange reactions during the leaching operation.

Two types of experimental control were exercised for the leaching test. The first type of control used the raw sludges for each residue category and was arranged in a similar fashion as the fixed sludges. The second type of control was within the experimental apparatus and utilized leaching columns in triplicate with and without the polypropylene filler beads for each leaching fluid.

Before loading the columns with samples, all materials were washed with a laboratory detergent followed by a rinse with dilute hydrochloric acid. The entire leaching apparatus was preleached with deionized water for a 1-week period at the design flow rate. The columns were loaded with the sample and initially filled from the bottom with leaching fluid to minimize air entrapment. No provisions were made to retard biological activity within the leaching apparatus, since the composition of the samples is such that biological activity is not expected to occur. The columns are translucent and observations of flow patterns as well as possible biological activity can be made.

## CHEMICAL PROPERTIES

Chemical properties of the leachates from the raw and fixed residues are classified into descriptive, organic, metals (cationic), and anionic analyses. The specific analyses included within these grouping are presented in Table 1. These parameters were selected to describe the chemical properties of the raw and fixed residues and to include all pollutants of specific interest within a residue category. All samples are analyzed for the descriptive parameters at each sampling time. The remaining chemical parameters were screened in all samples initially and analytical efforts were selectively reduced to a monitoring level in those cases where pollutant levels were low or considered insignificant. The ALG performed the bulk of these analyses and managed contract testing.

### Sampling

Sampling for leachates is scheduled for one year in a logarithmic fashion. Twelve samples are to be analyzed at total elapsed times of 7, 14, 21, 28, 42, 56, 86, 116, 146, 206, 266, and 356 days. The logarithmic sampling schedule best reflects leach column performance that would be predicted by mass transport theory.[4] Mass transport theory specifies a diffusion mechanism between the material surface and leaching solution. Although other reactions may be occurring, the data are evaluated by laboratory procedures and represent an "effective" diffusivity for a given pollutant. Behavior of these systems is generally characterized by a stable or a monotomically decreasing leach rate, approaching some limiting value. In this context, the initial sampling period becomes more critical than the later stages of leaching, and is best sampled by a logarithmic procedure.

Subsequent to sample analysis of the descriptive parameters, the samples are split into aliquots and preserved in relation to the analyses to be performed on the aliquot. The preservation scheme is described in Table 2. Those chemical parameters not specifically identified in Table 2 for preservation are either analyzed immediately after collection or require no preservation. All samples are held at 4°C until analyses are performed.

TABLE 1. CHEMICAL PROPERTIES

- Descriptive
  - Sample volume
  - pH[a]
  - Conductivity[a]
- Metals (cations)
  - Arsenic[a]
  - Berrylium[a,b]
  - Cadmium[a,b]
  - Calcium[a,b]
  - Chromium[a,b]
  - Copper[a,b]
  - Lead[a,b]
  - Magnesium[a,b]
  - Mercury[b]
  - Nickel[a,b]
  - Selenium[b]
  - Zinc[a,b]
- Organic
  - Chemical oxygen demand[a]
  - Total organic carbon[b]
- Anions
  - Chloride[a]
  - Cyanide[c]
  - Fluoride[a]
  - Nitrate[a,b]
  - Nitrite[a,b]
  - Sulfate[a,b]
  - Sulfite[a,b]

TABLE 2. SAMPLE PRESERVATION FOR CHEMICAL PROPERTIES

| Parameter | Method |
|---|---|
| Metals (cations) | Ultrex nitric acid[b] |
| Cyanide | Sodium hydroxide[b] |
| Total organic carbon | Hydrochloric acid[b] |
| Chemical oxygen demand | Sulfuric acid[b] |

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[a] Standard Methods for the Examination of Water and Wastewater, 13th Edition, American Public Health Association, Washington, D. C., (1971).

[b] Methods for Chemical Analysis of Water and Wastes, U. S. Environmental Protection Agency, Report No. EAP-625/6-74-003, (1974).

[c] Cyanide in Water and Wastewater, Technicon Industrial Method No. 315-74W, Technicon Company, (1974).

Sample preservation is used to allow some flexibility in programming the analytical scheduling to obtain maximum efficiency in the laboratory.

### Quality Control

To obtain assurance within the analytical program, an extensive quality control program has been implemented. This quality control program represents internal, intralaboratory, and extralaboratory procedures. The intralaboratory program includes spiked and reference samples within the column leachate samples. The internal program includes replicate determination and spike additions to representative samples. The extralaboratory program was coordinated between the ALG and the U.S.E.P.A. This assurance program primarily concentrates on the metals, since these pollutants represent the major group of interest within the project.

### Methods for Chemical Analysis

The methods adopted for chemical analyses were selected by the ALG and reviewed by the U.S.E.P.A. These are described by reference in Table 1.

The methods employed for metal analyses may be classified into two categories. All samples are first screened by flame atomic adsorption with the exception of arsenic, selenium, and mercury. If the results of these analyses are below detection limits, one replicate from the sample group is analyzed by atomic absorption using the heated graphite atomizer (HGA). The operating procedures that have been adopted eliminate the need for further sample handling to reach lower concentrations and rely directly on analytical procedures are presented in Table 3. Additionally, a portion of the samples are analyzed by argon plasma emission spectroscopy. This technique has a lower sensitivity than flame absorption for most metals, and serves as a check on other procedures. Since the major emphasis of the program lies with the metal analyses, a considerable effort has been expended to select techniques which maximize analytical throughput while minimizing sacrifices in precision and accuracy.

## PHYSICAL AND ENGINEERING PROPERTIES

In order to preclude any confusion in regard to the terminology used to describe the raw and fixed sludges, a brief definition of the properties and parameters cited herein is included in this chapter. All terms and tests are in standard use for the description and analysis of soils and/or concrete. Deviations from standard procedures are also noted within specific discussions; however, standard testing methods were generally adhered to for purposes of comparing results with literature values. Tests were performed on fixed residue specimens after a suitable curing period, as specified by the respective processors, had elapsed.

Table 3. OPERATING CONDITIONS FOR HEATED GRAPHITE ATOMIZER (HGA)

| | Element | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Be | Cd | Cr | Cu | Mg | Mn | Ni | Pb | Zn | As |
| Wave length, nm | 234.9 | 228.8 | 357.9 | 324.7 | 285.2 | 279.5 | 232.0 | 283.3 | 218.9 | 193.7 |
| Drying: | | | | | | | | | | |
| Temp, °C | 125 | 120 | 120 | 125 | 125 | 120 | 120 | 120 | 120 | 120 |
| Time, sec | 30 | 40 | 30 | 50 | 30 | 40 | 50 | 30 | 40 | 50 |
| Charring: | | | | | | | | | | |
| Temp, °C | 1200 | 400 | 1250 | 950 | 1200 | 1100 | 1200 | 500 | 400 | 1400 |
| Time, sec | 40 | 30 | 60 | 80 | 30 | 60 | 45 | 60 | 40 | 45 |
| Atomizing: | | | | | | | | | | |
| Temp, °C | 2800 | 2000 | 2600 | 2700 | 2000 | 2400 | 2500 | 2000 | 2500 | 2700 |
| Time, sec | 7 | 10 | 7 | 7 | 5 | 5 | 7 | 7 | 5 | 7 |

## Physical Properties

The following physical properties tests were performed during this study to determine the physical properties of the sludges:[3]

a. Grain size analysis

b. Specific gravity of solids

c. Bulk density

d. Dry density

e. Water content

f. Porosity/void ratio

g. Permeability

Grain Size Analysis-The grain size distribution of raw and fixed sludges was determined by hydrometer analysis. The hydrometer analysis is described in Appendix V of Engineer Manual (EM) 1110-2-1906[5] and in American Society for Testing Materials (ASTM) designation D 422-19.[6] This method, based on Stoke's Law, involves preparation of a suspension of sludge particles in water; measurement of the specific gravity of the suspension at specified time intervals; and correlation of settling velocity, particle diameter, and time in order to determine the distribution of grain sizes. The results of this test are plotted to give a particle size distribution curve and are used to assign the sludges a soil classification according to the Unified Soil Classification System (U.S.C.S.),[5] and according to the textural classification system employed by the U. S. Department of Agirculture (U.S.D.A.).

Specific Gravity-While there are three types of specific gravity defined for use in soils engineering, only the specific gravity of solids ($G_s$) applies to fine-grained material such as the FGD sludges. The specific gravity of a sludge is determined by dividing the unit weight of sludge by the unit weight of water. The test procedure as well as the soils definition are found in EM 1110-2-1906,[5] Appendix IV, and in ASTM D 854-58.[6]

Bulk Density-The bulk density is the air-dried unit weight, and is determined by weighing a sample of sludge of known volume and dividing the weight in pounds by the volume in cubic feet. Bulk density differs from dry density in that bulk density includes the weight of any interstitial water, while dry density is determined only after the water has been driven off by oven drying. The procedure for determining sample volume and weight can be found in Appendix II of EM 1110-2-190.[5]

Dry Density-The dry density or dry unit weight is defined as the weight of oven-dried sludge solids divided by the entire volume of sludge; and is generally expressed in pounds per cubic foot. Standard procedures for determining the weight and volume are presented in EM 1110-2-1906, Appendix II.[5]

Water Content-The water content, or moisture content, as the terms are interchangeable, is defined as the weight of water divided by the weight of dry solids in a sludge sample and is expressed as a percentage. A sludge sample of known weight is dried in an oven, and the weight loss is attributed to loss of interstitial water. This weight loss (water) divided by the weight of the dry sludge is the water content. Water content is determined by the method presented in EM 1110-2-1906[5] Appendix I and in ASTM D 2206-19.[6]

Porosity/Void Ratio-The void ratio of a specimen of sludge is defined as the ratio of the volume of the voids in the specimen to the volume of the solids in the specimen. Porosity is defined as the ratio of the volume of the voids of the specimen to the total volume of the specimen. Void ratio, e, is expressed as a decimal, while porosity, n, is expressed as a percentage. Porosity and void ratio are related to each other by the following equations:

$$n = \{e/(1 + e)\} \times 100\%$$

$$e = n/(1 - n);$$

and the pore volume within any specimen of known volume may be determined by by either of the following equations:

$$V_V = n \times V_T/100\%$$

$$V_V = e \times V_T/(1 + e),$$

where $V_V$ = pore volume, and

$V_T$ = total volume of specimen.

The standard procedure for determining void ratio and porosity are found in EM 1110-2-1906, Appendix II.[5]

Permeability-The permeability of a sample is defined as the fluid velocity which will pass through the sample under a given set of hydraulic conditions. The procedure for conducting the permability test is currently under investigation.

## Engineering Properties

In order to classify the fixed sludges according to their engineering properties, a number of standard engineering tests were performed on selected fixed sludges. These tests included the 15-blow compaction test, unconfined compression test, and cycles of wetting and drying.

15-Blow Compaction Test-The 15-blow compaction test simulates the compactive effort that might be expected from passing equipment over a placed landfill, while the Standard Proctor Compaction Test simulates the higher compactive effort required for fill placed in roadways and in dams. The 15-Blow Test was selected because it is felt that this compactive effort (> 400 FT-LB/CF) is more representative than that of the Standard Test

(12,200 FT-LB/CF) of the compaction that would be achieved for most of the productive uses of the fixed residues. A study conducted at the WES (Miscellaneous Paper 4-269) concluded that the maximum dry density was 3.4% higher for the standard test than for the 15-blow test. The 15-blow compaction test involves subjecting samples of sludge at different, known water contents to a specified compactive effort. After application of the compactive effort, the dry density of each sample is determined. The results of this test are presented in a graph of dry density versus water content. From this graph, the maximum dry density and optimum moisture content are determined. Test procedures appear in EM 1110-2-1906, Appendix VI[5] and in ASTM D 698-70.[6]

Unconfined Compression Test-The unconfined compression test is used to determine the uniaxial, unconfined compressive strength of a cohesive or cemented material. A cylindrical specimen is prepared and loaded axially until failure. The test results are presented as a graph of compressive stress versus axial strain. The compressive strength is taken as the peak compressive stress sustained by the sample. The modulus of elasticity (E), defined as the slope of the stress-strain curve, may also be determined from the results of the unconfined compression test. The standard testing procedure, found in Appendix XI of EM 1110-2-1906,[5] was followed except that a height-to-diameter ratio of 2.0 was used instead of 2.1.

Wet-Dry-Brush Test-This test is designed to evaluate the durability of fixed sludges by subjecting samples to 12 test cycles; each consisting of wetting, drying, and brushing operations. Results are presented as percent weight lost during the test. The standard wet-dry-brush test procedure is given in ASTM D 559-57.[6] Modifications to this procedure included the use of specimen diameters of three inches instead of four, and specimen heights of either four or six inches instead of 4.5 inches.

# SECTION IV

# RESIDUE FIXATION

## BACKGROUND

During Phase one of the project, nine fixation processes identified as A-I were selected as candidates for the program. A matrix was prepared assigning each process to either an industrial waste or FGD residue category, or both. A sufficient sample of each residue type was obtained from its respective source for the laboratory testing program. An aliquot of each sample was provided to each processor for evaluation at their laboratory according to the assignment matrix mentioned previously. The purpose for preliminary evaluation by the processors was to determine compatability between the fixation process and residue category and to establish optimum admixture ratios for each residue. Processors E and G delegated responsibility for this latter task to WES under the present program. The results of these evaluations will be discussed separately in this section.

After this preliminary evaluation phase, two processors, H and I, declined further participation in the project, generally for logistical reasons. The remaining processors agreed to fix the residues according to the assignments presented in Table 4. Process D, initially assigned to all residue categories, was eventually confined to one residue because of economic considerations. The remaining deletions occurred because the processors felt their fixation method would not be successful given a particular residue category. It is interesting to note that with the exception of one processor, all deletions occurred within the industrial residue categories. Speculation as to why these deletions were made cannot presently be made from a theoretical basis due to the complexities inherent in the fixation process chemistry and lack of specific information regarding certain processes.

At the conclusion of this preliminary evaluation task, the remaining processors were scheduled to perform fixation for the laboratory and physical testing at WES. This arrangement was made to allow project personnel to observe the actual fixation procedure and to maintain a degree of quality control consistent with all fixation methods. All fixation procedures included within the program required a curing time for their product. At the end of the curing time, the processors were invited to certify that fixation was adequate, and in some cases, to prepare samples for subsequent testing.

Table 4. PROCESS-RESIDUE ASSIGNMENT MATRIX

| Sludge category | Processes A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| 100[a] | X[b] | X | | | X | X | X |
| 200[c] | X | X | X | X | | | |
| 300[e] | X | X | †[d] | | | | |
| 400[f] | X | X | | | X | † | X |
| 500[g] | X | X | | | X | † | X |
| 600[h] | X | X | | | X | X | X |
| 700[i] | † | † | X | | | | |
| 800[j] | X | X | † | | | | |
| 900[k] | X | X | † | | | | |
| 1000[l] | X | X | | | X | † | X |

[a] Sludge 100 = FGD, lime process, eastern coal.
[b] X = Sludge actually fixed by processor and placed in column.
[c] Sludge 200 = Electroplating.
[d] + = Sludge evaluated by processor but not fixed for this study.
[e] Sludge 300 = Nickel/cadmium battery.
[f] Sludge 400 = FGD, limestone process, eastern coal.
[g] Sludge 500 = FGD, double alkali process, eastern coal.
[h] Sludge 600 = FGD, limestone process, western coal.
[i] Sludge 700 = Inorganic pigment.
[j] Sludge 800 = Chlorine production, brine sludge.
[k] Sludge 900 = Calcium fluoride.
[l] Sludge 1000= FGD, double alkali, western coal.

## GENERAL PROCEDURES

Residue samples obtained for the laboratory study were partitioned into several aliquots. A portion was used for preliminary evaluation by the processors, a portion was used for raw sludge chemical and physical testing, a portion was utilized for fixation, and the remainder of the sample was saved for supplementary testing. Sludge samples were stored in sealed, plastic containers under room conditions. Partitioning of one sample was adopted to minimize heterogeneity between sample usages which would hamper comparative evaluation of test data. All sample aliquots were mixed by a Lightning Mixer in required batch sizes prior to their use.

The fixation processes utilized in this project result in products which fall into two distinct groupings. The first group is a soil-like material which is highly variable in particle size and the second is a solid, continuous material. The procedure utilized for the first group consisted of fixing in a container and molding in square molds containing adequate volume for the fixed sample (48 x 48 x 3.5 inches). The molds were covered, and after curing the fixed sample was broken into smaller particle sizes and loaded into the columns. The second group of samples were molded in 3-inch diameter, paraffin lined tubes, 4 feet in length. Shorter tube lengths were used in some cases for convenience. After curing, the tubes were stripped and the resultant cores were placed in columns for chemical testing or subjected to physical tests. Specific deviation from these procedures will be discussed under sample fixation.

## SAMPLE FIXATION

The intent of this report section is to discuss the actual procedures utilized for fixation of the residues by process category. Included for each process is a discussion of the process plus the details relating to fixation as performed at WES. All weights presented in the succeeding tables for sludges are as wet weight, and for the remaining compounds on an as received basis.

Process A-Process A, which is patented, uses flyash and a lime additive to produce a pozzolan product. Fixation was performed on all sludges except 700. Bituminous flyash was used for the eastern coal FGD sludges, 100, 400, and 500, and for the industrial sludges; whereas, sub bituminous flyash was used for western coal FGD sludges 600 and 1000. The availability of flyash at power plants producing scrubber sludges is one advantage of this process. A fixed product with a high solids content (80%) is considered optimum, and dewatering the sludge often reduces the amount of flyash required, particularly for the scrubber sludges. All sludges that could be dewatered by decantation were dewatered at WES.

The sludges and fixation agents were mixed using a 5 cubic foot mortar mixer. The fixed product was then placed into cylindrical molds, covered, and allowed to cure for 30 days. Inspection of the fixed specimens revealed that curing in the molds under a dry environment had produced cracks, a situation which the processor felt was not representative of this process; therefore, a decision was made to repeat the fixation process. Because of time limitations and convenience to the processor the second fixation was conducted at the processor's laboratories. In this case, the specimens were placed in shorter tubes (3 in. x 16 in.) and cured under humid conditions to prevent drying. The fixed specimens were then shipped to WES for chemical and physical testing. The processor chose not to reveal the specific additive-to-sludge ratios for proprietary reasons; however, the percent of dry sludge solids for each fixed specimen is presented in Table 5. These mixes are slightly different from larger scale preparations because of the need to work with small molds. In a field scale operation placement and consolidation of the sludges would likely be done with construction equipment, hence, requiring a stiffer, lower moisture content mix.

Table 5. PROCESS A-FORMULATION FOR RESIDUE FIXATION

| Residue category | Percent dry sludge solids |
|---|---|
| 100 | 49 |
| 200 | 25 |
| 300 | 21 |

Table 5.-(continued)

| Residue category | Percent dry sludge solids |
|---|---|
| 400 | 49 |
| 500 | 49 |
| 600 | 57 |
| 800 | 41 |
| 900 | 37 |
| 1000 | 35 |

Process B-Process B, which is patented, uses two additives to produce a soil-like material. The proportions of reagents used determine the hardness of the fixed product. The hardness of the end product is determined either by ultimate use or the quantity of reagents required to affect pollutant immobilization. In most cases a soil-like material, which is more economical, is produced.

The sludge and reagents were mixed in 9 to 14 gallon batches using a Lightning Mixer. This provided mixing equivalent to that produced by prototype equipment which includes an aerated, continuously stirred reactor and a series of recirculating and transfer pumps designed to provide complete mixing of the reagents and sludge. The solids, volumes of sludge, and weight of additives for the nine fixed sludges are given in Table 6. Molds 4 feet square by 3.5 inches were used to hold the fixed sludge for curing. A polyethylene cover was used during the curing period (12 days) to prevent excessive drying. The fixed specimens were broken into smaller particle sizes and placed in the column without compaction.

Process C-Process C uses an organic resin plus other additives in a polymerization process to form a solid rubber-like material. The organic resin is a patented product. Table 7 describes the formulation used for each batch of fixed material prepared. The reagents were manually mixed with the sludge using a paddle stirrer. The mixture was then immediately poured into cylindrical molds after mixing and allowed to cure.

Process D-Process D is an encapsulation method utilizing a resin to form an agglomerate which is subsequently surrounded by a 0.25- inch plastic jacket fused to the agglomerate. The process requires a dry residue for fixation which was provided by WES to the processor's laboratory. Fixation was performed outside WES because of the specialized equipment needed to produce fixed samples.

The fixed residue samples provided to WES were cylindrical in shape, 3 inches in diameter and 4 inches in height, each containing approximately 250 grams of dry residue. These cylinders were used as received for all chemical and physical testing.

Table 6. PROCESS B--FORMULATION FOR RESIDUE FIXATION

| Residue Category | Percent solids | Volume fixed (gallons) | Weight of additives (lb/gal of sludge) |
|---|---|---|---|
| 100 | 37.9 | 28 | 1.80 |
| 200 | 34.0 | 28 | 1.10 |
| 300 | 41.2 | 23 | 0.90 |
| 400 | 35.7 | 28 | 1.80 |
| 500 | 43.3 | 27 | 2.10 |
| 600 | 32.1[a] | 25 | 2.10 |
| 800 | 59.7 | 20 | 1.80 |
| 900 | 44.9 | 28 | 0.90 |
| 1000 | 39.6 | 25 | 1.80 |

[a] Dewatered from 13.4% TS to 32.1% TS for fixation.

Table 7. PROCESS C-FORMULATION FOR RESIDUE FIXATION

| Item | Residue category | |
|---|---|---|
| | 200 | 700 |
| Weight of sludge (g) | 4800 | 4800 |
| Weight of additives (g) | 2400 | 2880 |

Process E-Process E uses two readily available commercial materials (additives) to convert waste sludge into a hardened mass similar to concrete. This particular processor has not devoted extensive research toward this process because of its conventional nature and the expense of the process, which may prevent wide application in the field for large volumes of sludge.

A representative of the company visited WES and furnished guidance on the method for determining the optimum formulations for fixation of the five FGD sludges. Laboratory preparation of specimens for evaluation of the leaching characteristics was demonstrated. The procedure used for determining the optimum formulation is as follows:

a. Mix small samples (100-200 g) of each sludge with various combinations of additive A and B.

b. Pour each fixed specimen into a mold and allow the specimens to cure two days.

c. Place each specimen in a 1500 ml beaker, add 1000 ml deionized water, and stir slowly for 24 hours.

d. Analyze the leachate for calcium, sulfates, and conductivity.

e. Select the optimum formulation based on minimum leachability and integrity of the sample (specimens which disintegrated upon contact with water were discarded).

A minimum of twelve sludge-additive A, B, combinations for each sludge were evaluated. Results for the six best combinations are presented in Table 8. The optimum formulation was based strictly on minimum leachability without regard to economic considerations.

Fixed samples for the column study were prepared in 20 gallon batches. Mixing was produced with a Lightening Mixer, except for sludge 500, where a 4 cubic foot concrete mixer was used. The processor had suggested that a concrete mixer be used for mixing the reagents with the sludge; however, the Lightning Mixer provided more efficient blending of the materials. Conditions for fixation of the five sludges are given in Table 9. After thoroughly mixing the reagents with the sludge, the mixture was poured into cylindrical molds and allowed to cure for four weeks at room conditions before testing.

Table 8. PROCESS E-BENCH SCALE LEACHATE DATA

| Sludge number | Additive A -sludge ratio | Additive B -sludge ratio | Calcium (ppm) | Sulfate (ppm) | Conductivity (μmhos/cm) |
|---|---|---|---|---|---|
| 100 | 0.33 | 0.33 | 2300 | 800 | NA[a] |
| 100 | 0.34 | 0.51 | 5200 | 210 | NA |
| 100 | 0.42 | 0.42 | 1900 | 660 | NA |
| 100 | 0.43 | 0.26 | 2000 | 658 | NA |
| 100 | 0.50 | 0.25 | 1800 | 668 | NA |
| 100 | 0.52 | 0.17 | 2100 | 598 | NA |
| 400 | 0.31 | 0.08 | 240 | 510 | $.03\text{x}10^3$ |
| 400 | 0.32 | 0.16 | 240 | 166 | $1.99\text{x}10^3$ |
| 400 | 0.31 | 0.31 | 190 | 186 | $1.68\text{x}10^3$ |
| 400 | 0.39 | 0 | 240 | 212 | $2.02\text{x}10^3$ |
| 400 | 0.40 | 0.08 | 220 | 268 | $2.58\text{x}10^3$ |
| 400 | 0.38 | 0.15 | 250 | 185 | $2.11\text{x}10^3$ |
| 500 | 0.20 | 0.10 | 130 | 710 | $5.20\text{x}10^3$ |
| 500 | 0.20 | 0.20 | 120 | 781 | $4.95\text{x}10^3$ |
| 500 | 0.20 | 0.40 | 610 | 565 | $5.00\text{x}10^3$ |
| 500 | 0.50 | 0 | 170 | 700 | $4.80\text{x}10^3$ |
| 500 | 0.50 | 0.10 | 120 | 610 | $5.20\text{x}10^3$ |
| 500 | 0.50 | 0.20 | 160 | 540 | $4.20\text{x}10^3$ |
| 600 | 0.20 | 0.35 | 83 | 57 | $1.06\text{x}10^3$ |
| 600 | 0.20 | 0.60 | 83 | 42 | $1.12\text{x}10^3$ |
| 600 | 0.40 | 0.35 | 30 | 39 | $1.02\text{x}10^3$ |
| 600 | 0.50 | 0.20 | 100 | 37 | $1.31\text{x}10^3$ |
| 600 | 0.50 | 0.35 | 55 | 37 | $1.11\text{x}10^3$ |
| 600 | 0.50 | 0.50 | 48 | 34 | $0.99\text{x}10^3$ |

Table 8.-(continued)

| Sludge number | Additive A -sludge ratio | Additive B -sludge ratio | Calcium (ppm) | Sulfate (ppm) | Conductivity (umhos/cm) |
|---|---|---|---|---|---|
| 1000[b] | 0.40 | 0.10 | NA | 805 | $5.59x10^3$ |
| 1000 | 0.50 | 0.10 | NA | 542 | $5.10x10^3$ |
| 1000 | 0.50 | 0.25 | NA | 438 | $4.62x10^3$ |
| 1000 | 0.60 | 0.10 | NA | 390 | $4.60x10^3$ |
| 1000 | 0.60 | 0.25 | NA | 344 | $4.52x10^3$ |
| 1000 | 0.60 | 0.40 | NA | 394 | $4.41x10^3$ |

[a] No analysis.
[b] All 1000 samples included 0.25 parts water per part sludge.

Table 9. PROCESS E-FORMULATION FOR RESIDUE FIXATION

| Sludge no. | Weight of sludge (lb) | Additive A -sludge ratio | Additive B -sludge ratio | Water-sludge ratio | Mixing time (min) | Type of mixer |
|---|---|---|---|---|---|---|
| 100 | 145 | 0.50 | 0.25 | 0 | 10 | Lightning |
| 400 | 160 | 0.31 | 0.31 | 0 | 10 | Lightning |
| 500 | 193 | 0.50 | 0.20 | 0 | 45 | Concrete |
| 600 | 160 | 0.40 | 0.35 | 0 | 15 | Lightning |
| 1000 | 121 | 0.60 | 0.40 | 0.25 | 15 | Lightning |

Process F-Process F mixes a patented additive, designated herein as Reagent F, with a sludge at optimum pH to settle the solids in the slurry. The solid mass cures in the presence of the supernatant for approximately 30 days, forming a hardened clay-like material.

Table 10 lists the formulations and fixation data for sludges 100 and 600. The pH adjustment was performed and Reagent F, a dry powder, was added slowly and allowed to mix thoroughly with the sludge. The fixed samples were poured into cylindrical molds. All the tubes were then enveloped in polyethylene tents to maintain a humid environment for curing the specimens. The relatively large amount of free liquid which accompanied the fixed solids in the tubes resulted in some leakage of liquid through the walls of the mold thereby reducing the amount of free supernatant over the samples. This loss of liquid would not occur under field conditions; however, the samples remained moist and cured to the satisfaction of the processor.

Process G-Process G is a fixation technique in which waste sludge is mixed with an additive which is a waste product from a manufacturing industry, and the pH of the mixture is adjusted to an optimum value. An advantage of this process is that the additive and the compound used to adjust pH are both normally waste materials The processor evaluated various combinations of materials in his own laboratory and then chose the two most promising mixtures (labelled a and b) for bench-scale demonstration at WES. After the fixed specimens had cured to a constant weight (20 to 30 days) they were leached with deionized water for 72 hours. The conductivity was periodically measured during the leaching process and reached an equilibrium after 24 hours. The results of leachate analysis after 72 hours are given in Table 11. The best mixture was selected on the basis of minimum leachability of calcium, cadmium, and sulfates. Table 12 describes the fixation conditions for the five sludges fixed at WES. The fixed sludges were cured in 20 x 3 inch cylindrical molds for ten weeks prior to testing.

Table 10. PROCESS F-FORMULATION FOR RESIDUE FIXATION

| Item | Sludge number 100 | 600 |
|---|---|---|
| Total weight (lb) | 229 | 276 |
| Percent solids | 36 | 40 |
| Percent reagent F | 10 | 10 |
| Wt. reagent F. (lb) | 8.5 | 11 |
| Final pH | 12.9 | 12.4 |
| Mixing time (min) | 30 | 30 |

Table 11. PROCESS G-BENCH SCALE LEACHATE DATA

| Sludge number | Calcium (mg/1) | Sulfate (mg/1) | Cadmium (μg/1) | Specimen weight (g) |
|---|---|---|---|---|
| 100a | 500 | 3250 | 0.8 | 160 |
| 100b | 490 | 2400 | 1.1 | 143 |
| 400a | 380 | 1760 | 1.8 | 140 |
| 400b | 490 | 3850 | 2.6 | 118 |
| 500a | 510 | 4400 | 3.8 | 164 |
| 600a | 470 | 3750 | 5.0 | 129 |
| 600b | 510 | 3960 | 3.3 | 130 |
| 1000a | 500 | 7000 | 5.5 | 161 |
| 1000b | 450 | 6000 | 6.0 | 146 |

Table 12. PROCESS G-FORMULATION FOR RESIDUE FIXATION

| Sludge number | Weight sludge (lb) | Weight additive (lb) | Final wt. (lb) | Percent solids |
|---|---|---|---|---|
| 100 | 74 | 74 | 223 | 36 |
| 400 | 55 | 55 | 178 | 13 |
| 500 | 58 | 58 | 288 | 46 |
| 600 | 50 | 50 | 190 | 20 |
| 1000 | 84 | 84 | 360 | 38 |

## SAMPLE DESCRIPTION

To visualize the effect of fixation upon selected residues, a photographic record has been prepared for comparison. This record is presented for residue categories 100 through 1000 in Figures 1 through 10, respectively. The effect of fixation on physical characteristics is obvious, the resultant reduction in surface area to volume ratio should intuitively provide superior chemical performance during leach testing. Most materials seem to possess reasonable structural properties on the basis of appearance; physical properties will be discussed in detail in a subsequent section.

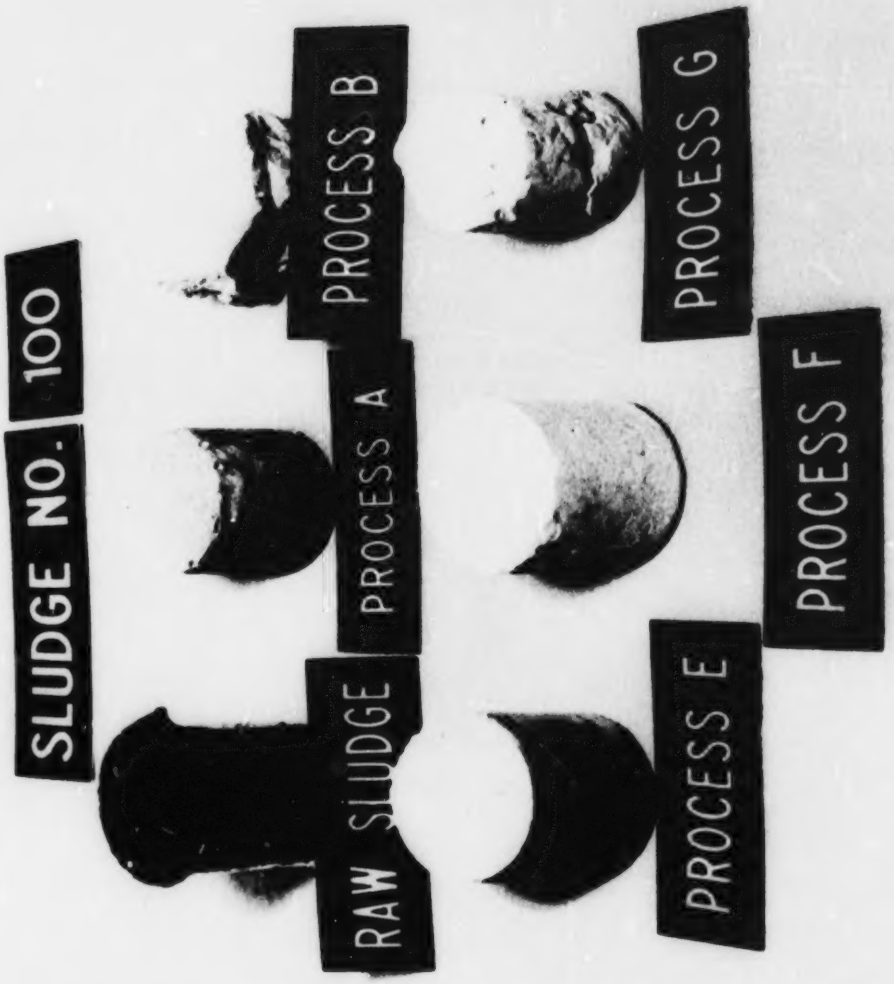

SLUDGE NO. 100
RAW SLUDGE
PROCESS A
PROCESS B
PROCESS E
PROCESS F
PROCESS G

Figure 1. Raw and fixed residues, Number 100.

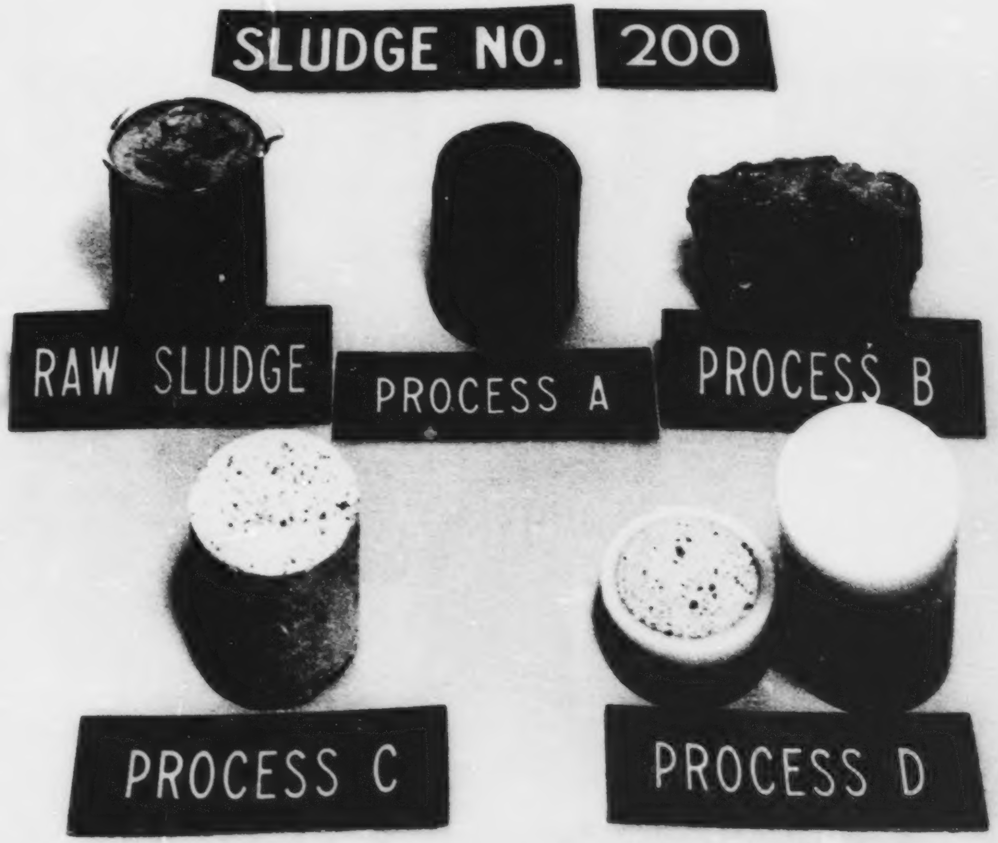

SLUDGE NO. 200
RAW SLUDGE
PROCESS A
PROCESS B
PROCESS C
PROCESS D

Figure 2. Raw and fixed residues, Number 200.

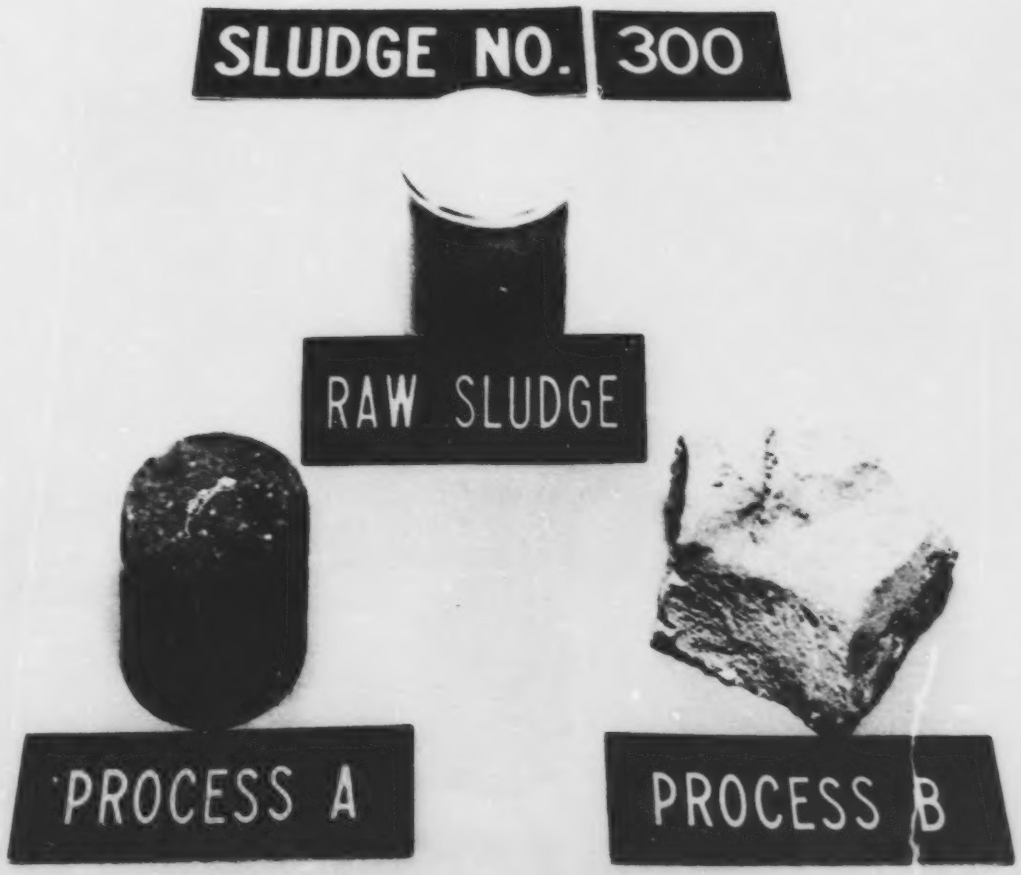

SLUDGE NO. 300
RAW SLUDGE
PROCESS A
PROCESS B

Figure 3. Raw and fixed residues, Number 300.

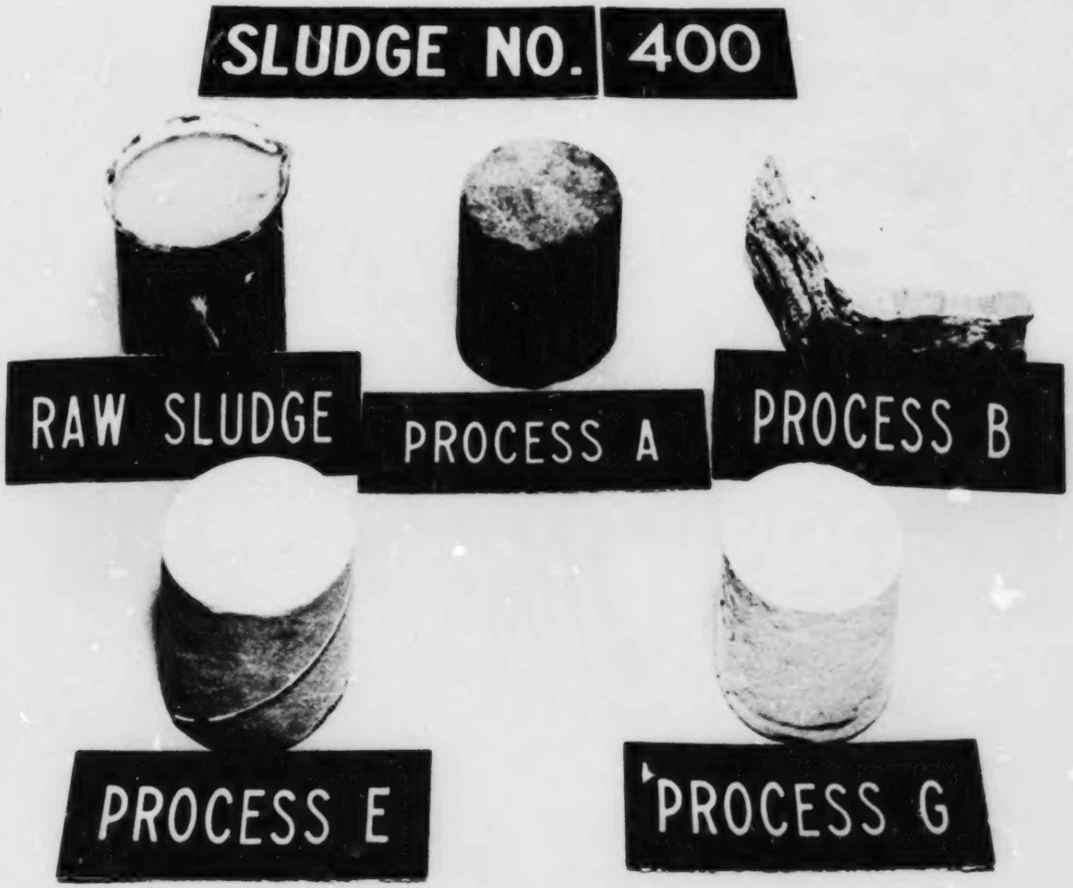

SLUDGE NO. 400
RAW SLUDGE
PROCESS A
PROCESS B
PROCESS E
PROCESS G

Figure 4. Raw and fixed residues, Number 400.

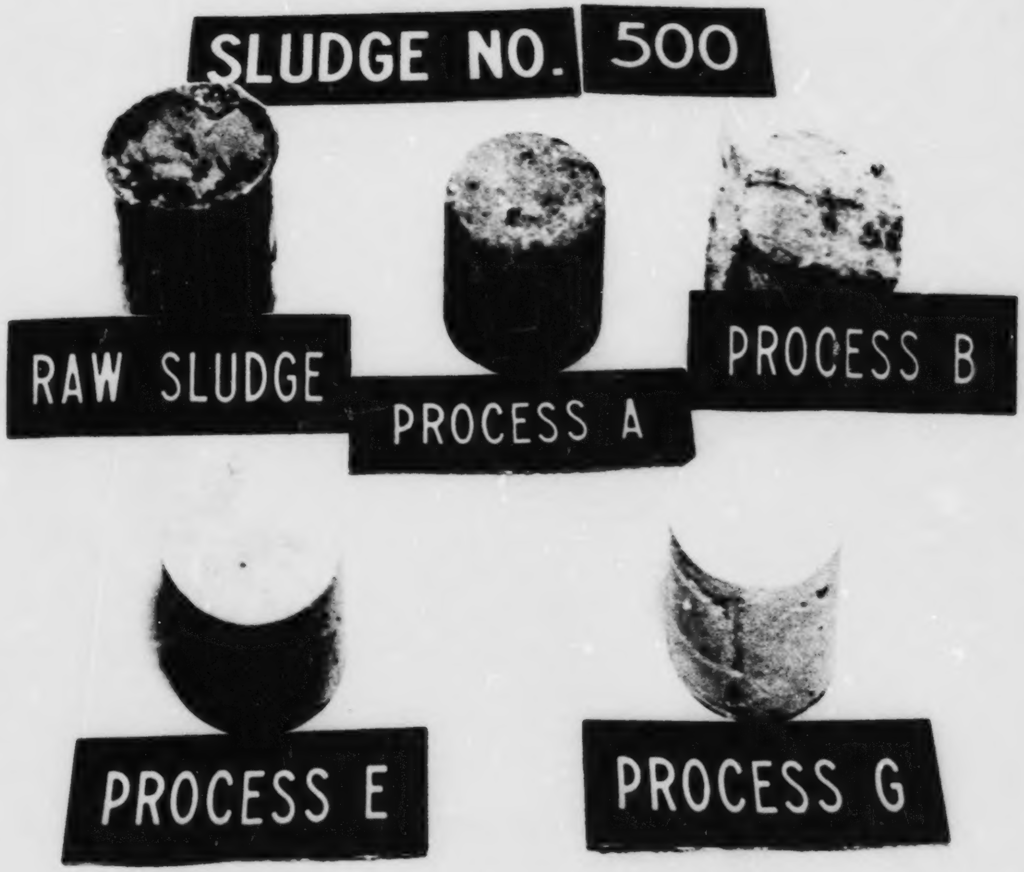

SLUDGE NO. 500
RAW SLUDGE
PROCESS A
PROCESS B
PROCESS E
PROCESS G

Figure 5. Raw and fixed residues, Number 500.

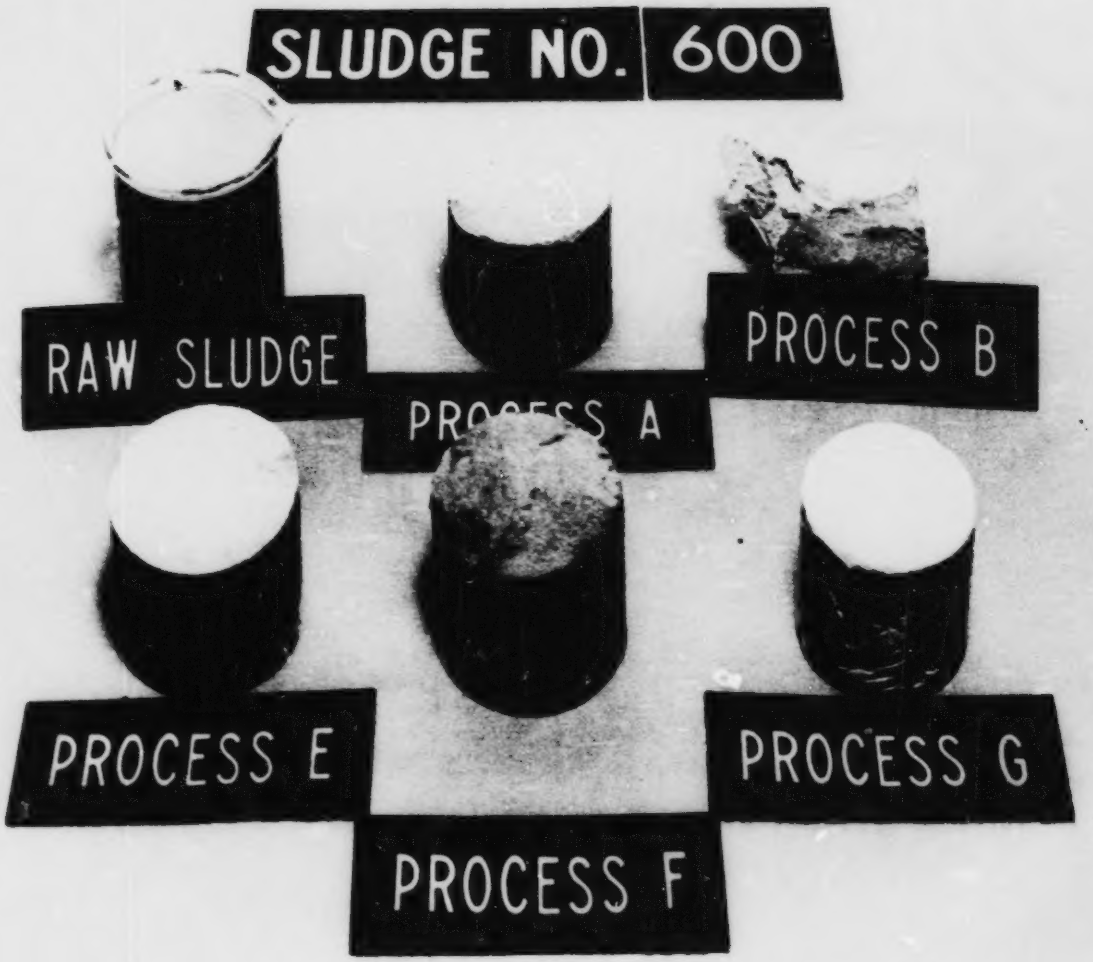

SLUDGE NO. 600
RAW SLUDGE
PROCESS A
PROCESS B
PROCESS E
PROCESS F
PROCESS G

Figure 6. Raw and fixed residues, Number 600.

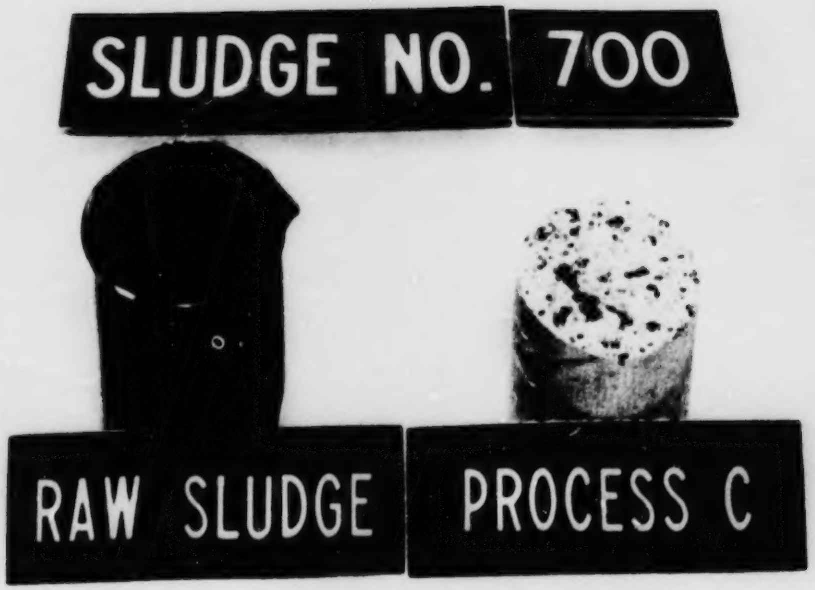

SLUDGE NO. 700
RAW SLUDGE
PROCESS C

Figure 7. Raw and fixed residues, Number 700.

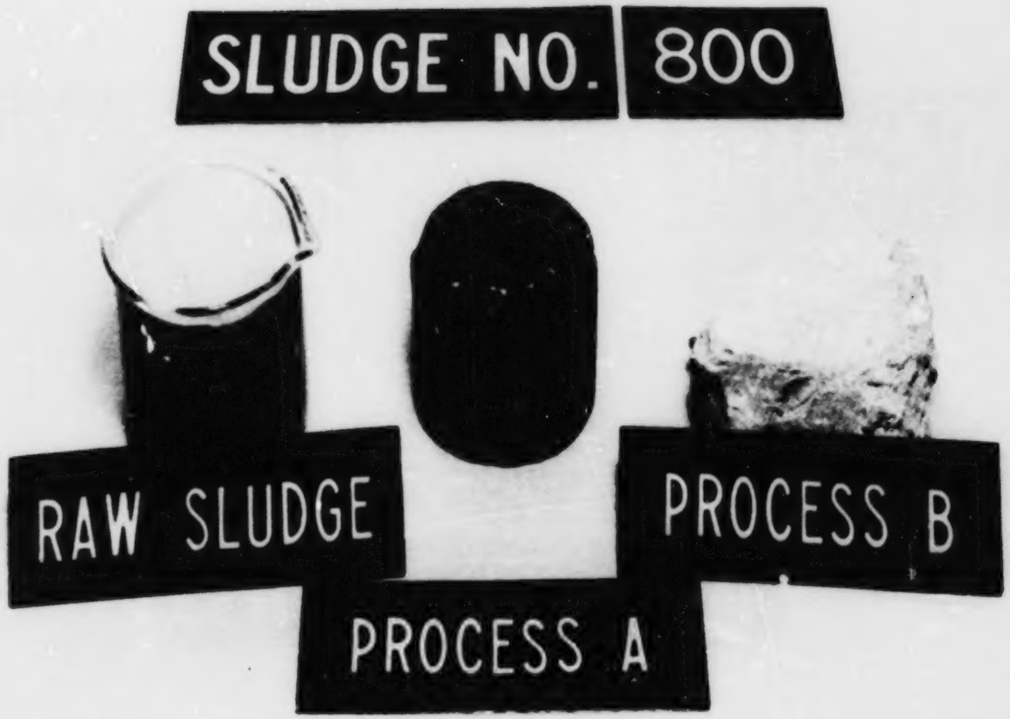

SLUDGE NO. 800
RAW SLUDGE
PROCESS A
PROCESS B

Figure 8. Raw and fixed residues, Number 800.

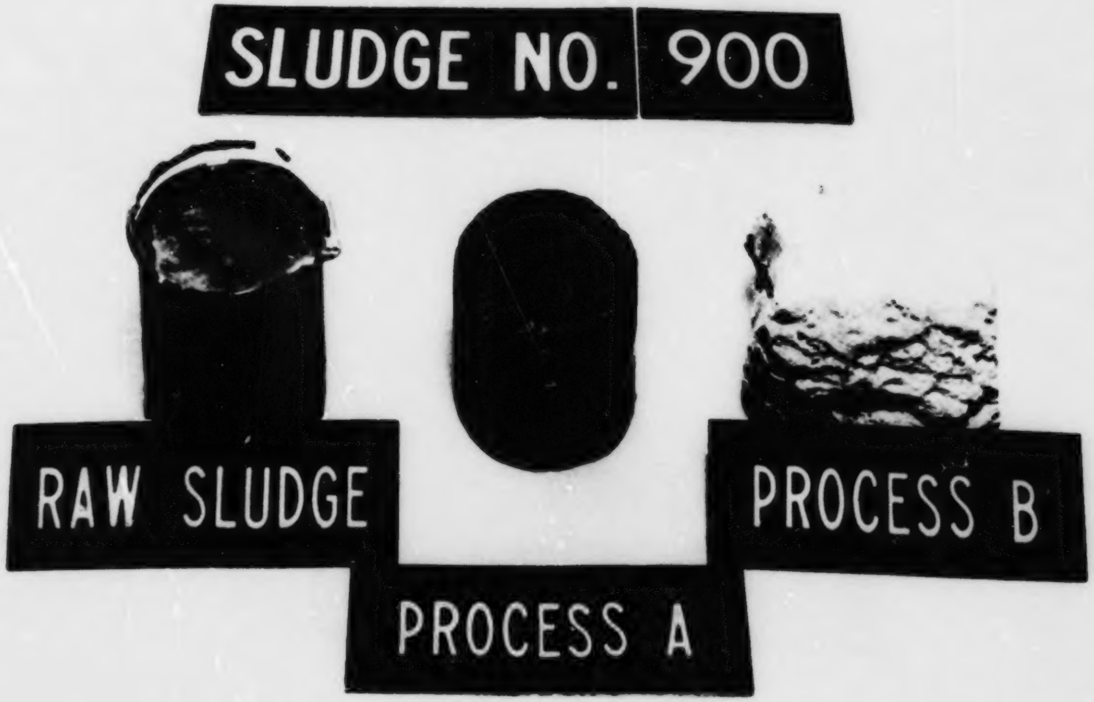

SLUDGE NO. 900
RAW SLUDGE
PROCESS A
PROCESS B

Figure 9. Raw and fixed residues, Number 900.

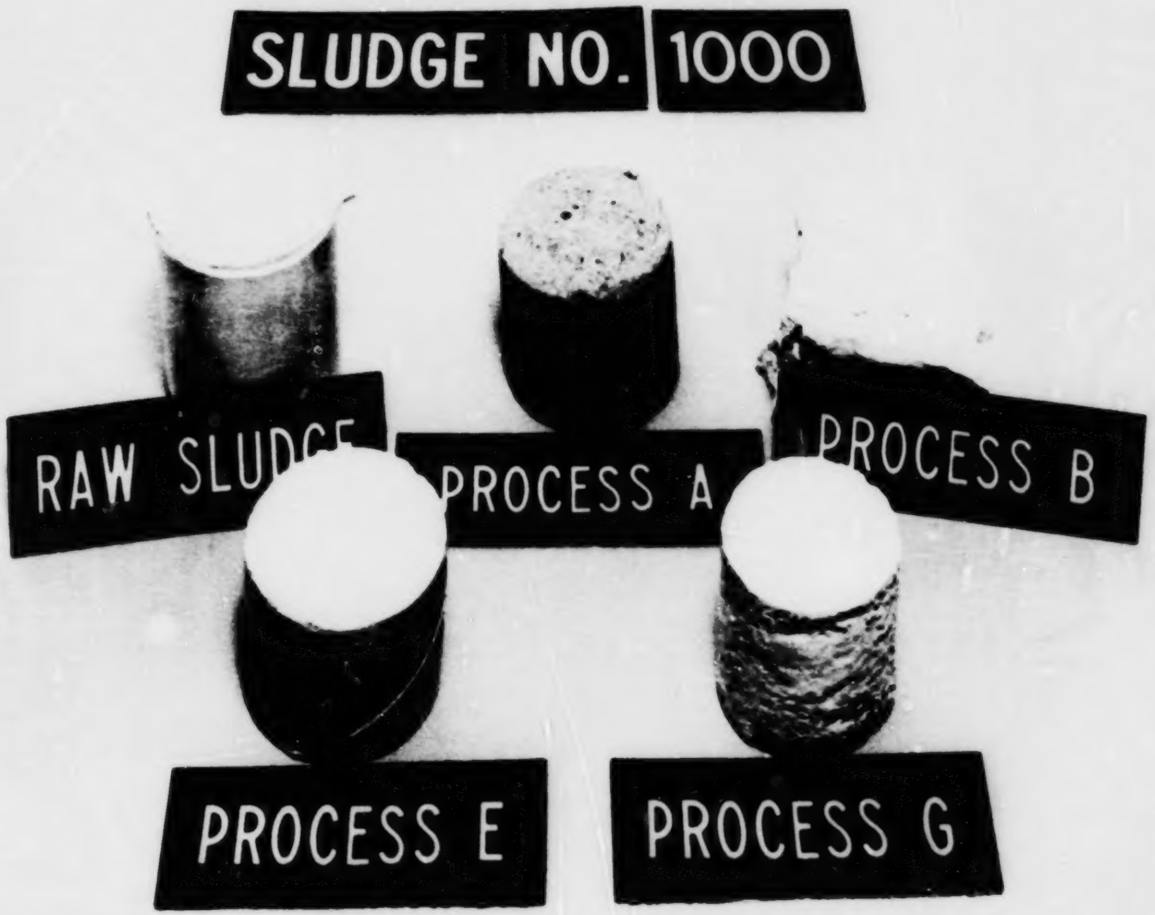

SLUDGE NO. 1000
RAW SLUDGE
PROCESS A
PROCESS B
PROCESS E
PROCESS G

Figure 10. Raw and fixed residues, Number 1000.

# SECTION V

# PHYSICAL AND ENGINEERING PROPERTIES

## BACKGROUND

One approach to the characterization of chemically fixed hazardous sludges involves the evaluation of their physical and engineering properties, as determined by standard tests. Physical properties describe the particle structure of the sludge, while engineering properties are used to evaluate the sludge as a mass and to predict its reaction to applied loads. An evaluation of the effects of the fixation processes on the properties of the sludges is made possible by conducting physical and engineering properties tests on samples of sludges both before and after treatment with the chemical fixing agents, and comparing the results. Furthermore, the properties of the fixed sludges may be compared with regard to the type of treatment process used. Additional characterization of the fixed sludges is possibly by comparing the properties of the sludges with typical values of the properties of other, more familiar materials such as soil-cement, concrete, soils, and some common mineral and rock types.

The purpose of this section is to characterize chemically fixed sludges as fully as possible by evaluating the physical and engineering properties of the sludges. The properties of the raw sludges are presented first for comparative purposes. The physical and engineering properties of the fixed sludges are presented next according to the procedure utilized. The last part of this section deals with potential productive uses of fixed sludges; however, more detailed investigations are necessary before the potential of the fixed sludges for productive uses can be fully evaluated. The physical and engineering properties presented herein are the result of standard tests which have been discussed previously (Section III); consequently, these properties reflect only those characteristics determined by these tests.

## PROPERTIES OF RAW SLUDGES

Physical properties of the untreated sludges are determined by conducting eight standard tests, the results of which appear in Table 13. The R-designated materials are the raw sludges, while the remaining are fixed sludges, each bearing the specific fixation processes prefix letter designation. In comparison with soils, the raw sludges are generally of low density, with the exception of R-300; and except R-200, all are of low water content. The specific gravities however, are comparable to soils, indicating that structural rearrangement of the particles should result in densities of

## TABLE 13. PHYSICAL AND ENGINEERING PROPERTIES OF RAW AND FIXED SLUDGES

| PHYSICAL PROPERTIES | | | | | | | | ENGINEERING PROPERTIES | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | 15-Blow compaction test | | Unconfined compression test | | | |
| Material | Specific gravity[a] | Bulk[b] density (lb/cf) | Oven-dry[b] unit wt (lb/cf) | Water[b] content (%) | Porosity[b] (%) | Void[b] ratio | Wet-dry % wt.loss | Max dry density[a] lb/cf | Optimum moisture content[a] % | Undrained shear strength (psi) | Unconfined compressive strength (psi) | Modulus of elasticity[b,d] (psi) | Coefficient of permeability (cm/sec) |
| R-100 | 2.45 | 51.7 | 50.0 | 3.3 | 67.3 | 2.059 | NA | NA | NA | NA | NA | NA | NA |
| R-200 | 3.27 | 63.5 | 42.4 | 49.6 | 79.2 | 3.815 | NA | NA | NA | NA | NA | NA | NA |
| R-300 | 3.99 | 157.2 | 153.1 | 2.7 | 38.5 | 0.627 | NA | NA | NA | NA | NA | NA | NA |
| R-400 | 2.73 | 63.1 | 61.1 | 3.2 | 64.2 | 1.789 | NA | NA | NA | NA | NA | NA | NA |
| R-500 | 2.90 | 52.3 | 47.1 | 11.0 | 74.0 | 2.844 | NA | NA | NA | NA | NA | NA | NA |
| R-600 | 2.67 | 89.0 | 85.8 | 3.7 | 48.5 | 0.943 | NA | NA | NA | NA | NA | NA | NA |
| R-700 | 3.00 | 55.5 | 50.9 | 9.1 | 72.8 | 2.679 | NA | NA | NA | NA | NA | NA | NA |
| R-800 | 2.82 | 64.3 | 57.4 | 12.1 | 67.4 | 2.067 | NA | NA | NA | NA | NA | NA | NA |
| R-1000 | 2.95 | 47.4 | 45.3 | 4.6 | 75.4 | 3.065 | NA | NA | NA | NA | NA | NA | NA |
| B-100 | 2.68 | 77.0 | 41.4 | 85.9 | 75.3 | 3.041 | NA | 41.0 | 91.0 | NA | NA | NA | NA |
| B-200 | 2.94 | 87.1 | 44.1 | 97.6 | 76.0 | 3.162 | NA | 46.5 | 86.5 | NA | NA | NA | NA |
| B-300 | 3.75 | 93.2 | 47.1 | 97.9 | 79.9 | 3.970 | NA | 74.3 | 47.0 | NA | NA | NA | NA |
| B-400 | 2.98 | 79.4 | 36.2 | 119.5 | 80.5 | 4.139 | NA | 48.5 | 74.0 | NA | NA | NA | NA |
| B-500 | 2.94 | 90.8 | 52.2 | 74.0 | 71.6 | 2.516 | NA | 49.5 | 72.0 | NA | NA | NA | NA |
| B-600 | 2.75 | 79.6 | 40.7 | 95.6 | 76.3 | 3.218 | NA | 40.4 | 89.8 | NA | NA | NA | NA |
| B-800 | 2.88 | 105.9 | 80.6 | 31.4 | 55.2 | 1.231 | NA | 73.6 | 39.1 | NA | NA | NA | NA |
| B-900 | 2.76 | 86.2 | 52.0 | 65.7 | 69.8 | 2.313 | NA | 59.8 | 53.8 | NA | NA | NA | NA |
| B-1000 | 2.81 | 81.5 | 47.1 | 73.0 | 73.2 | 2.724 | NA | 49.8 | 75.0 | NA | NA | NA | NA |
| C-200 | 1.81 | 75.4 | 50.2 | 50.2 | 55.6 | 1.251 | c | NA | NA | 374 | 747 | 17,000 | NA |
| C-700 | 1.80 | 65.7 | 43.2 | 52.0 | 38.5 | 1.601 | c | NA | NA | 154 | 309 | 10,000 | NA |
| E-100 | 2.64 | 101.4 | 89.5 | 13.0 | 45.7 | 0.801 | 15.80 | NA | NA | 1,287 | 2,574 | 450,000 | NA |
| E-400 | 2.73 | 82.7 | 76.1 | 8.7 | 55.4 | 1.240 | 15.00 | NA | NA | 360 | 719 | 126,000 | NA |
| E-500 | 2.77 | 99.3 | 88.2 | 12.6 | 49.0 | 0.961 | 10.85 | NA | NA | 1,110 | 2,220 | 310,000 | NA |
| E-1000 | 2.67 | 82.7 | 82.0 | 0.9 | 50.8 | 1.033 | 6.60 | NA | NA | 687 | 1,374 | 245,000 | NA |
| F-600 | 2.60 | --- | --- | --- | --- | --- | --- | -- | 198 | 396 | --- | --- | NA |

[a] Value determined from one specimen.
[b] Average value determined from three specimens.
[c] Disintegrated during first cycle.
[d] Tangent of "straight" portion of stress-strain curve.
NA -- Not applicable.

the same magnitude as those of soils. The high porosities of the sludges give an indication of how loosely packed the sludge particles are; in fact, the total volume of most samples included more than 60 percent voids.

On the basis of the grain size distributions, Figures 11-13, the raw sludges were classified as silt (ML) under the Unified Soil Classification System; and as silt and silt loam with the U.S.D.A. system. While no engineering properties tests were conducted on raw sludge samples, general characteristics may be predicted. The grain size distributions for the raw sludges show that a high percentage of the particles pass the number 200 sieve usually indicative of low permeability ($< 10^{-4}$cm/sec). Strength is also expected to be low. Soils of low density are generally so loosely packed that little intergranular friction is developed, and shear strengths are correspondingly low in the absence of cementation.

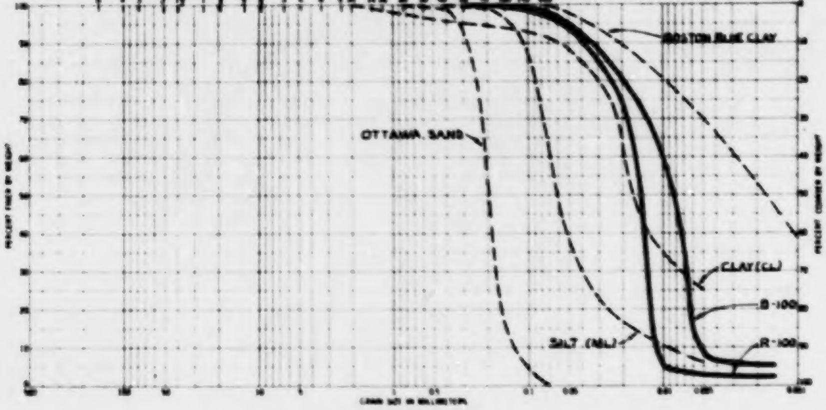
Prior to treatment, sludges were characterized by low densities and low water content, leading to the anticipation of low shear strength (2-8 psi) and low permeability. ($< 10^{-4}$ cm/sec). Porosity is high and improvement in the quality of the sludges should be accomplished by restructuring the particle matrix to provide a tighter packing arrangement. Comparison of the physical properties of the raw sludges to soils is presented in Table 14.

## PHYSICAL PROPERTIES OF FIXED SLUDGES

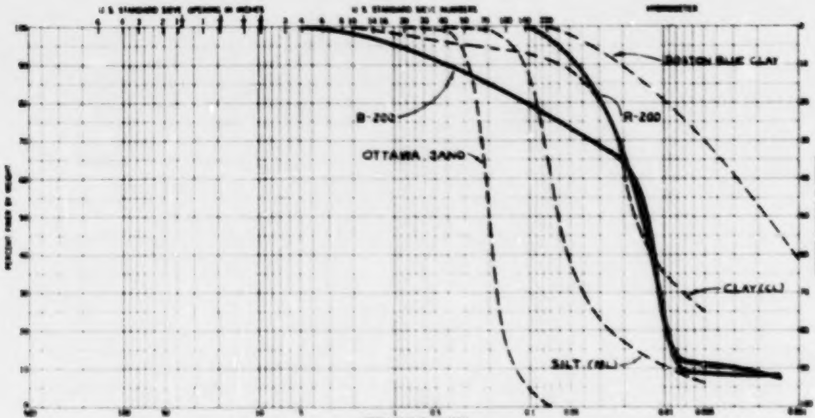
### Grain Size Distribution and Soil Classification

The grain size distribution of nine sludges treated with process B and of one sample treated with process F were determined. Each fixed sludge was given a soil classification of either silt (ML) or silty sand (SM) under the U.S.C.S system. Sludges fixed with process B were classified loam, or fine sandy loam under the U.S.D.A system. The grain size curves of the fixed sludges were plotted on the same graphs as the curves for the corresponding raw sludges, as shown in Figures 11-13 and Figure 14.

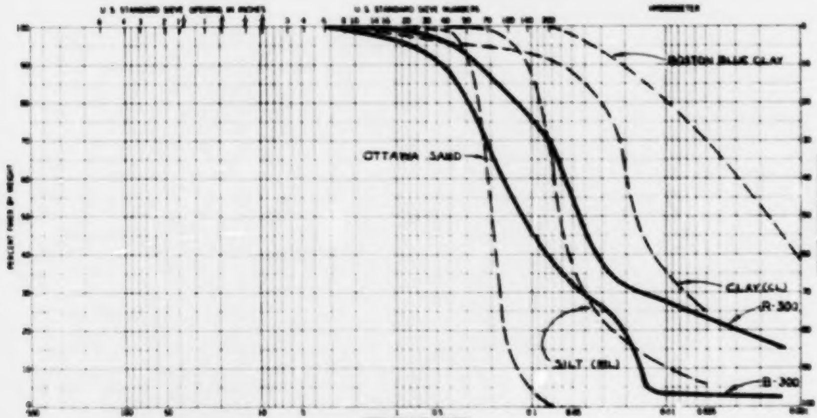
Comparison of the grain size curves for sludges fixed with process B with those of raw sludges, Figure 11-13, shows that the process had little effect on the distribution of particle sizes. Particle sizes of the fixed sludges remain in the same range as those of the raw sludges. It was anticipated that identical treatment (B) of all sludges might result in some change in particle size. The change in gradation, though slight, was not uniform for all sludges fixed with treatment B. There was no change for sludges 500 and 800; the curves for raw and treated sludges plot almost together, crossing in several places. Treatment of some sludges, though, resulted in a finer gradation than the corresponding raw sludges (100, 400, and 600); and the other treated sludges, B-200, B-300, B-900, and B-1000, proved to have a coarser gradation than the corresponding untreated sludges. All B-treated sludges remain, however, similar to the raw sludges in texture, and are similar to silty soils.



SLUDGE 100

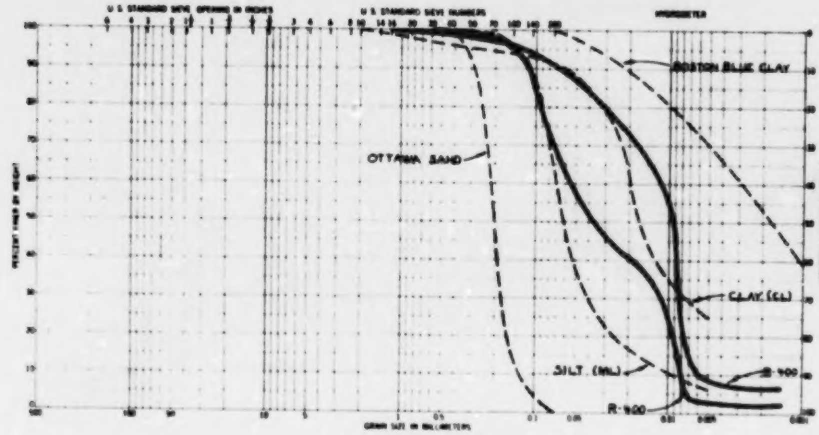


SLUDGE 200

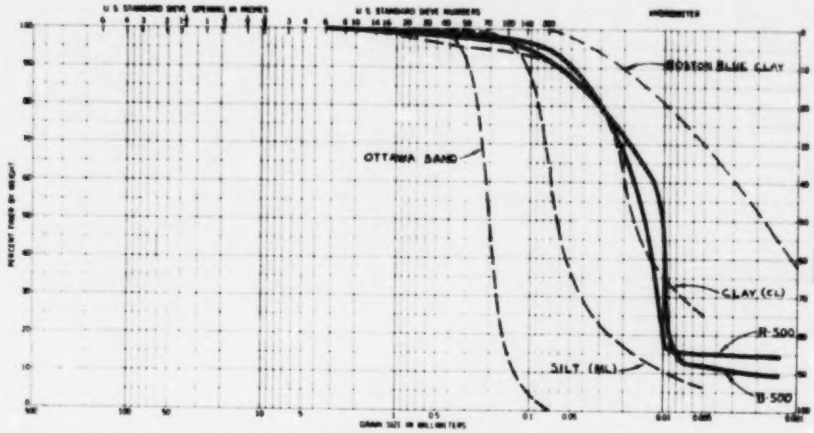


SLUDGE 300

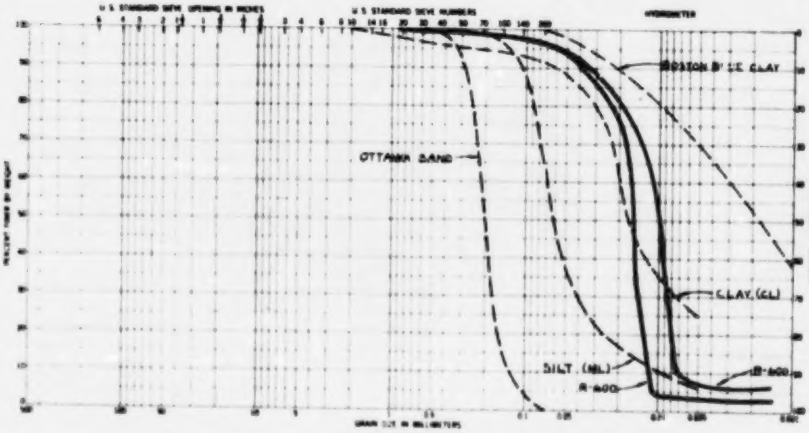
Figure 11. Grain size distributions, raw and fixed sludges (100, 200, and 300).



**SLUDGE 400**

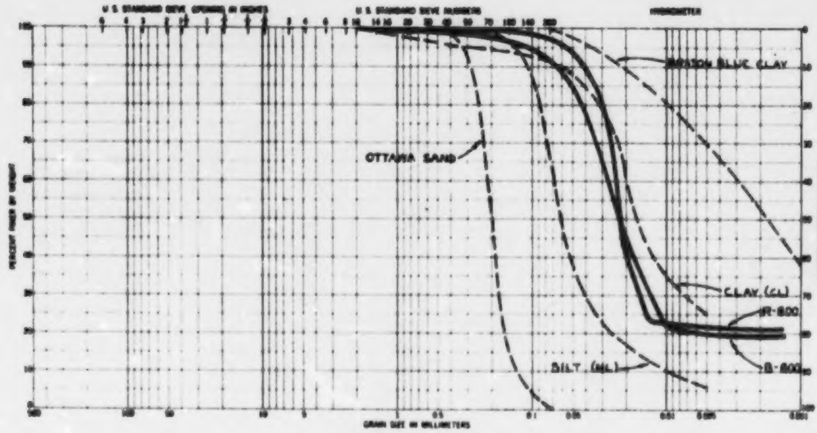


**SLUDGE 500**

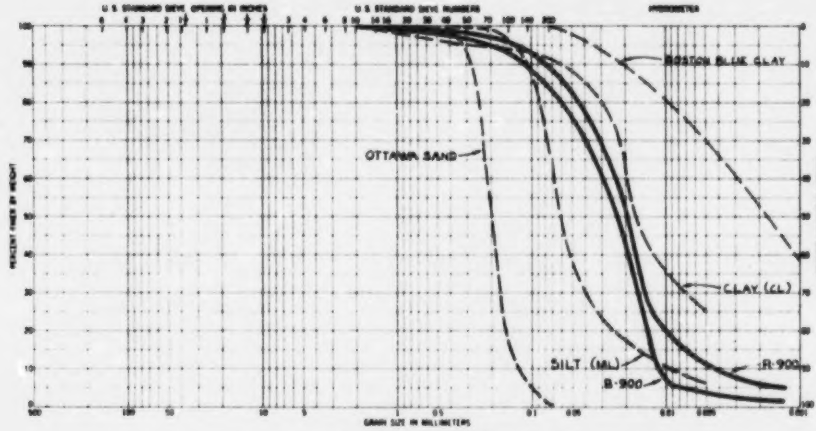


**SLUDGE 600**

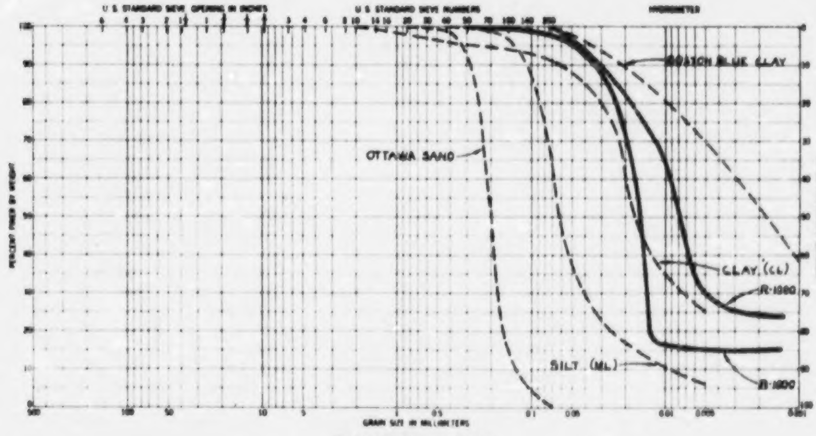
Figure 12. Grain size distributions, raw and fixed sludges (400, 500, and 600).



**SLUDGE 800**



**SLUDGE 900**

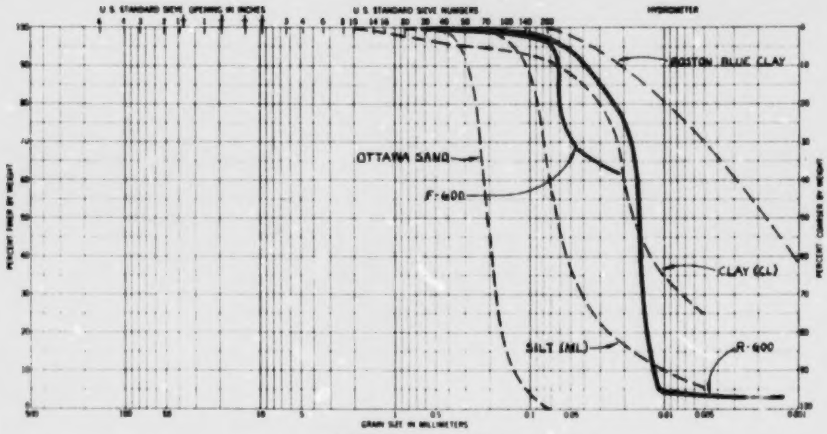


**SLUDGE 1000**

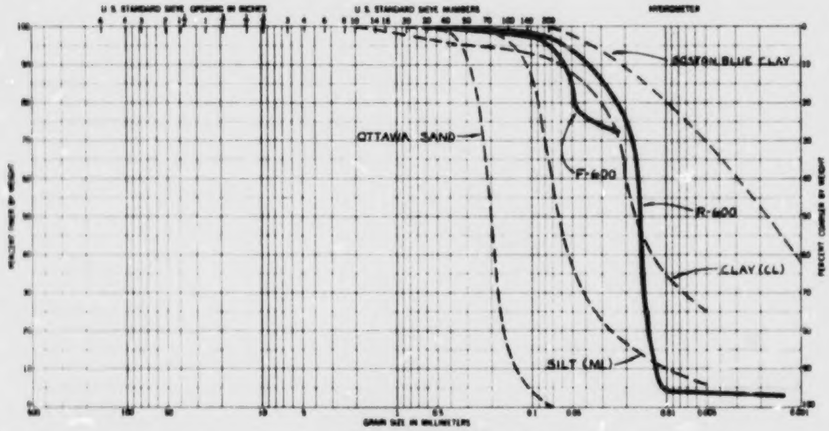
Figure 13. Grain size distributions, raw and fixed sludges (800, 900, 1000).

## TABLE 14. COMPARISON OF PHYSICAL PROPERTIES AMONG SOILS, RAW SLUDGES, AND FIXED SLUDGES

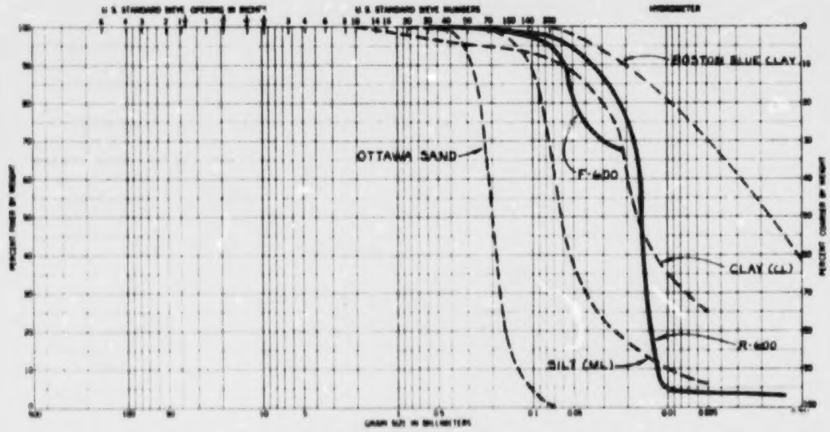
| Materials | Properties | | | | | | |
|---|---|---|---|---|---|---|---|
| | Specific Gravity | Porosity % | Void Ratio | Maximum Dry Density (PCF) | Natural Water Content (%) | Optimum Moisture Content (%) | Permeability (cm/sec) |
| Well-graded dense sand | 2.65 | 30 | 0.43 | 138 | 16 | 12 | $10^{-1}$ |
| Soft inorganic clay | 2.70 | 55 | 1.2 | 112 | 45 | 20 | $10^{-8}$ |
| Soft organic clay | 2.60 | 75 | 3.0 | 100 | 110 | 30 | $10^{-6}$ |
| R-100 | 2.45 | 67.3 | 2.059 | | 3.3 | | |
| R-200 | 3.27 | 79.2 | 3.815 | | 49.6 | | |
| R-300 | 3.99 | 38.5 | 0.627 | | 2.7 | | |
| R-400 | 2.73 | 64.2 | 1.789 | | 3.2 | | |
| R-500 | 2.90 | 74.0 | 2.844 | | 11.0 | | |
| R-600 | 2.67 | 48.5 | 0.943 | | 3.7 | | |
| R-700 | 3.00 | 72.8 | 2.679 | | 9.1 | | |
| R-800 | 2.82 | 67.4 | 2.067 | | 12.1 | | |
| R-900 | 2.74 | 70.0 | 2.334 | | 5.3 | | |
| R-1000 | 2.95 | 75.4 | 3.065 | | 4.6 | | |
| B-100 | 2.68 | 75.3 | 3.041 | 41.0 | 85.9 | 91.0 | |
| B-200 | 2.94 | 76.0 | 3.162 | 46.5 | 97.6 | 86.5 | |
| B-300 | 3.75 | 79.9 | 3.97 | 74.3 | 97.9 | 47.0 | |
| B-400 | 2.98 | 80.5 | 4.139 | 47.2 | 119.5 | 84.0 | |
| B-500 | 2.94 | 71.6 | 2.516 | 49.5 | 74.0 | 72.0 | |
| B-600 | 2.75 | 76.3 | 3.218 | 40.4 | 95.6 | 89.8 | |
| B-800 | 2.88 | 55.2 | 1.231 | 73.6 | 31.4 | 39.1 | |
| B-900 | 2.76 | 69.8 | 2.313 | 59.8 | 65.7 | 53.8 | |
| B-1000 | 2.81 | 73.2 | 2.724 | 49.8 | 73.0 | 75.0 | |



**SLUDGE 600**



**SLUDGE 600**



**SLUDGE 600**

Figure 14. Grain size distributions, raw and fixed sludges (600).

### Specific Gravity

In general, treatment of the sludges resulted in little change in specific gravity. Some values were slightly higher after treatment, and some were slightly lower, but changes were not process-dependent. Treatment of sludges 200 and 700 with process C resulted in specific gravities considerably (40 to 50 percent) lower than those of the raw sludges. All specific gravities are reported in Table 14. Values remain in the range of common minerals and soils, as shown in Figure 15 and in Table 14.[8,9]

### Bulk Density

Bulk density, or air-dry unit weight, did not exhibit as wide a range of values after treatment as before treatment. The range of values for all treated sludges is 65.7 LB/CF to 105.9 LB/CF, while for raw sludges values ranged from 47.4 LB/CF to 157.2 LB/CF. There were some large reductions, as well as some increases, in bulk density resulting from treatment; but none appeared to be dependent upon the type of treatment process.

### Dry Density

Dry density, oven-dry unit weight, was generally lower after treatment by process B, considerably higher after fixation by process E, and not process-dependent with process C. The dry densities of sludges fixed by process E are in the range of light-weight clays and silts. All values of dry density for fixed sludges are presented in Table 13.

### Water Content

A large increase in water content resulted from treatment of sludges by process B. Water contents for B-treated sludges ranged from 2 to 37 times those of the raw sludges. One of the fixed sludges, C-200, experienced only a slight increase in water content (0.6%) while C-700 had a sevenfold increase. Sludges with process E remained at low water contents in the range of the raw sludges. All water contents are shown in Table 13.

### Porosity/Void Ratio

Porosity and void ratio, reported in Table 13 remained about the same after fixation with process B. Processes C and E resulted in lower values of porosity and void ratio. Comparisons of sludges, raw as well as fixed, with soils in terms of void ratio and porosity are presented in Figure 16[8] and Table 14.[9,10]

### Permeability

At the time of this report, no permeability data were available.

## ENGINEERING PROPERTIES OF FIXED SLUDGES

Three standard engineering properties tests were conducted on selected fixed sludges. The 15-Blow Compaction Test was conducted on nine samples of sludges

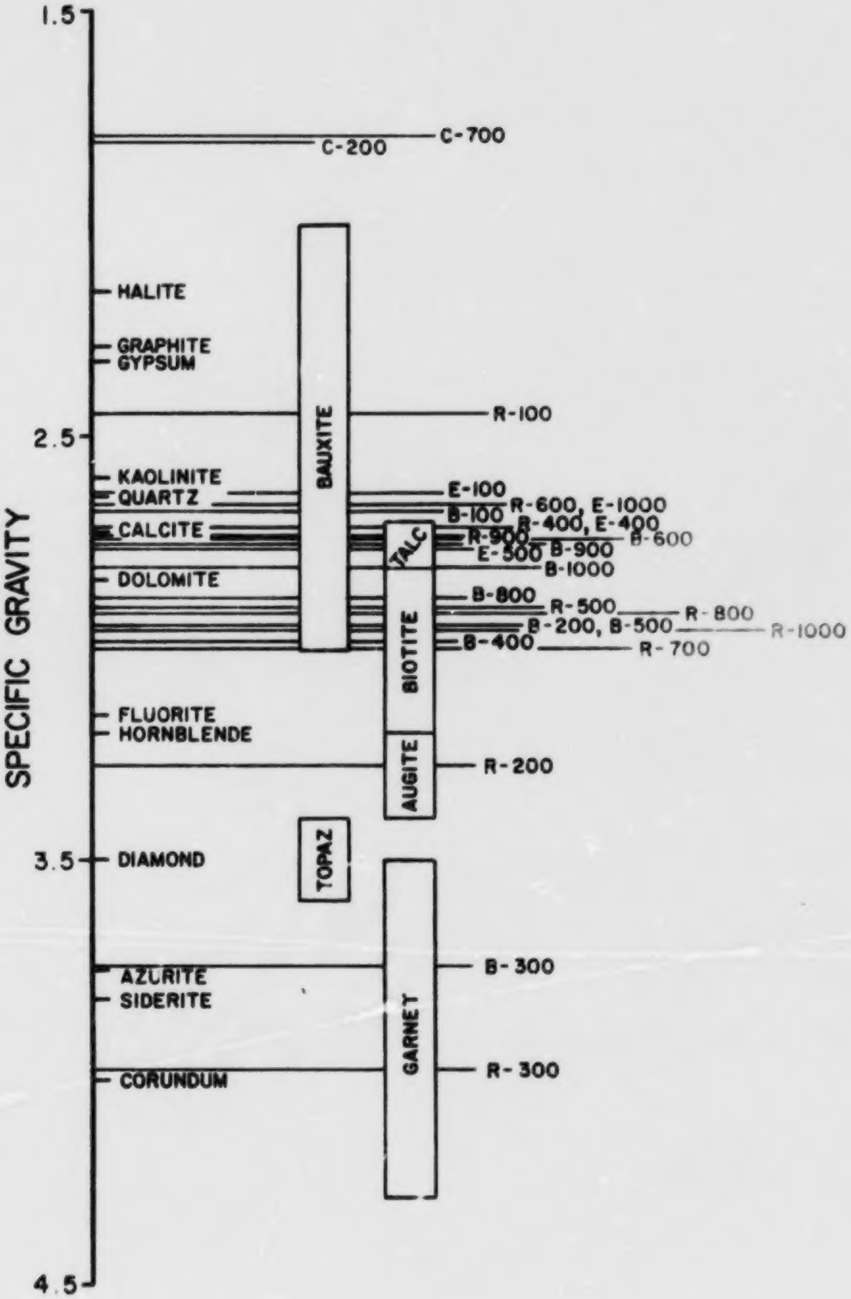


Figure 15. Specific gravities of common materials compared with raw and fixed sludges.

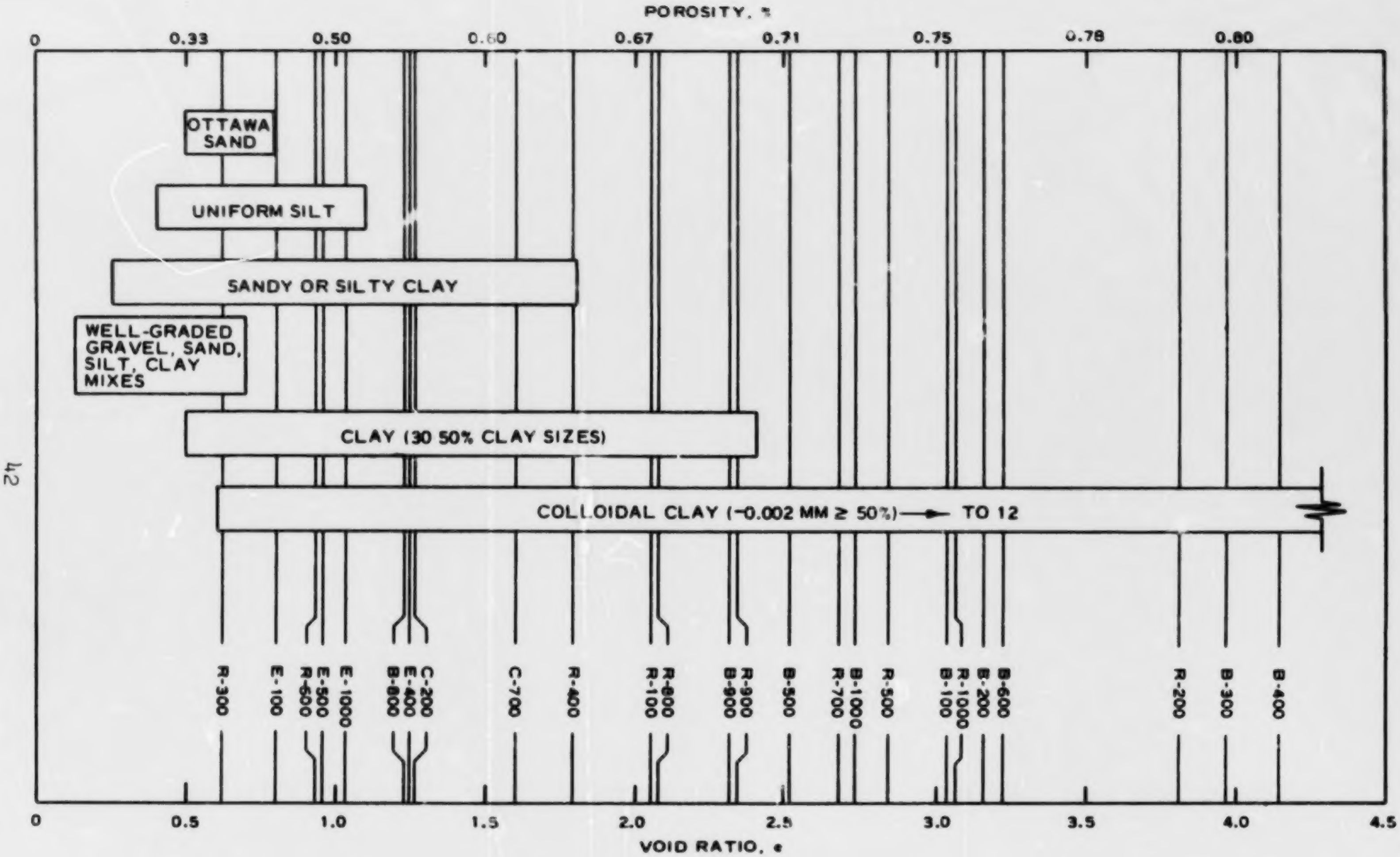


Figure 16. Porosity and void ratio of soils compared with raw and fixed sludges

fixed with process B to determine the density-moisture relationships of the fixed sludges. The compressive strengths of specimens of sludges treated by processes C, E, and F were determined by performing the Unconfined Compression Tests. Durability of sludges fixed with processes C and E was determined by the wet-dry-brush test.

## Compaction Test

Results of the compaction test, reported in Tables 13 and 14 and in Figure 17, show that sludges fixed with process B exhibit low dry densities and high optimum moisture contents (OMC), when compared to basic soil types. The high values of OMC might be partially attributed to the presence of hydrates within the sludge matrix. A comparison of the dry densities of sludges fixed with process B before and after the application of the compactive effort of the 15-blow compaction reveals that in some cases (B-300, B-400, and B-900) a more dense material resulted. Furthermore, samples B-100 and B-600 were unaffected by the test; and two samples, B-500 and B-800 had higher densities before the compactive effort. This comparison, presented in Figure 18 indicates that some difficulty may be anticipated in field compaction of certain fixed sludges.

## Unconfined Compression Test

The compressive strengths of samples of sludges fixed with processes C, E, and F were determined by an unconfined compression test. Additionally, the modulus of elasticity was determined from the stress-strain curve for each sludge treated. Sludges fixed with processes C or E lost their soil consistency and became quite hard; undergoing a cementation process. Compressive strengths of sludges fixed with process E, Table 14, are comparable to those of low strength concrete (3000 psi at 28 days). Figures 19 and 20[12,13] show comparisons between concrete and sludges fixed by process E, and between soil-cement and samples fixed by process E, respectively. The stress-strain curves also show that sludges fixed with process E are brittle; failure occurred at low strains. Sludges fixed with processes C and F however, failed at very high strains indicating an elastic consistency, though compressive strengths were lower than the sludges fixed with process E. Figures 21 and 22 show the stress-strain curves for fixed sludges. These curves were used to determine the modulus of elasticity, E, of the samples. In this case, E was determined to be the tangent of the "straight" portion of the stress-strain curve, as illustrated in Figure 23.[14] The values for E are reported in Table 13.

## Wet-Dry-Brush Test

This test of durability was performed on samples fixed by processes C and E. The sludges fixed by process E performed fairly well, as compared to the sludges fixed by process C, which failed during the first cycle. Figures 24 and 25 show the samples after 4 and 12 cycles respectively. The weight loss determined for samples fixed by process E are reported in Table 13.

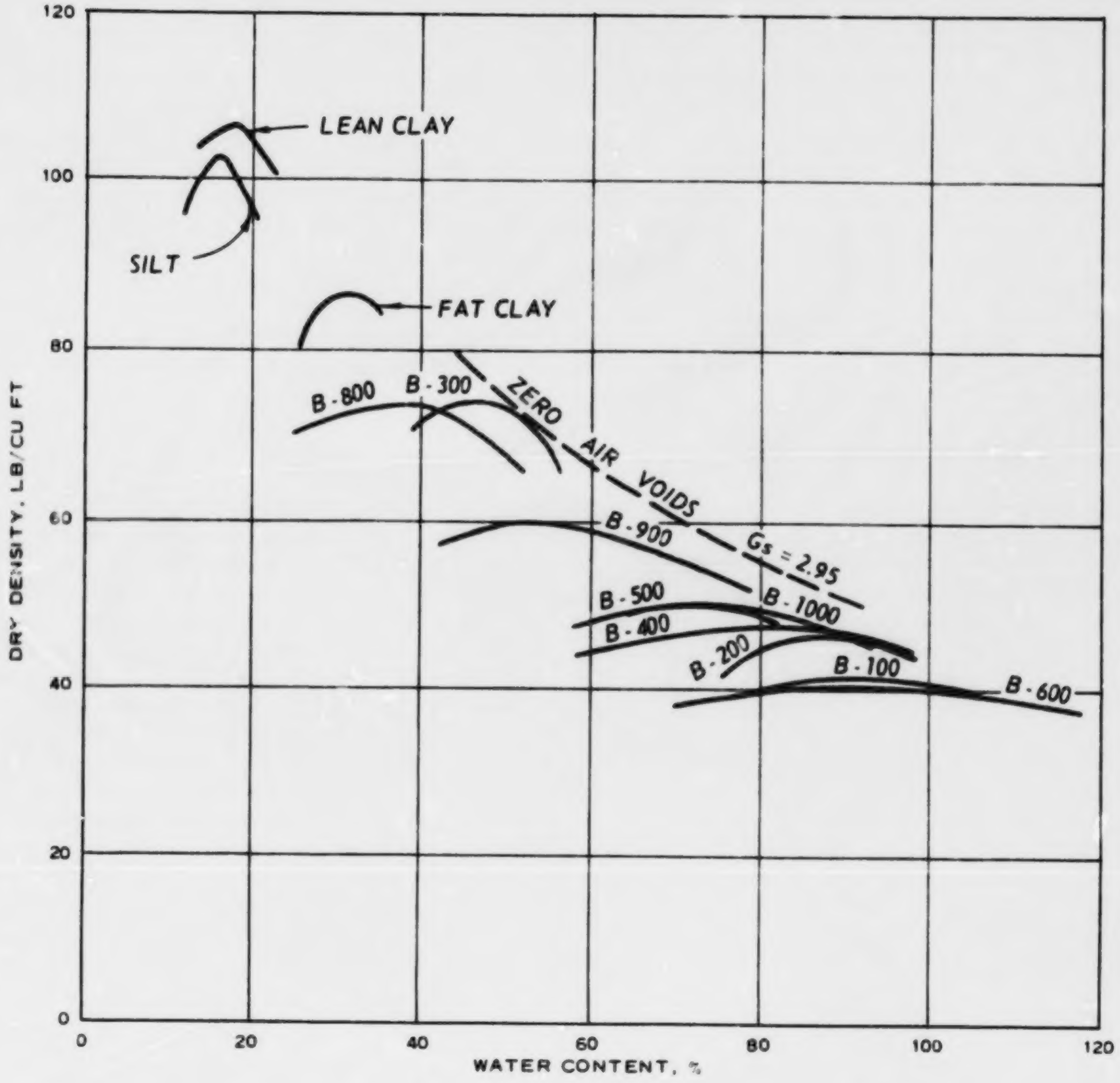


Figure 17. Compaction test, comparison of soils with residues fixed by process B

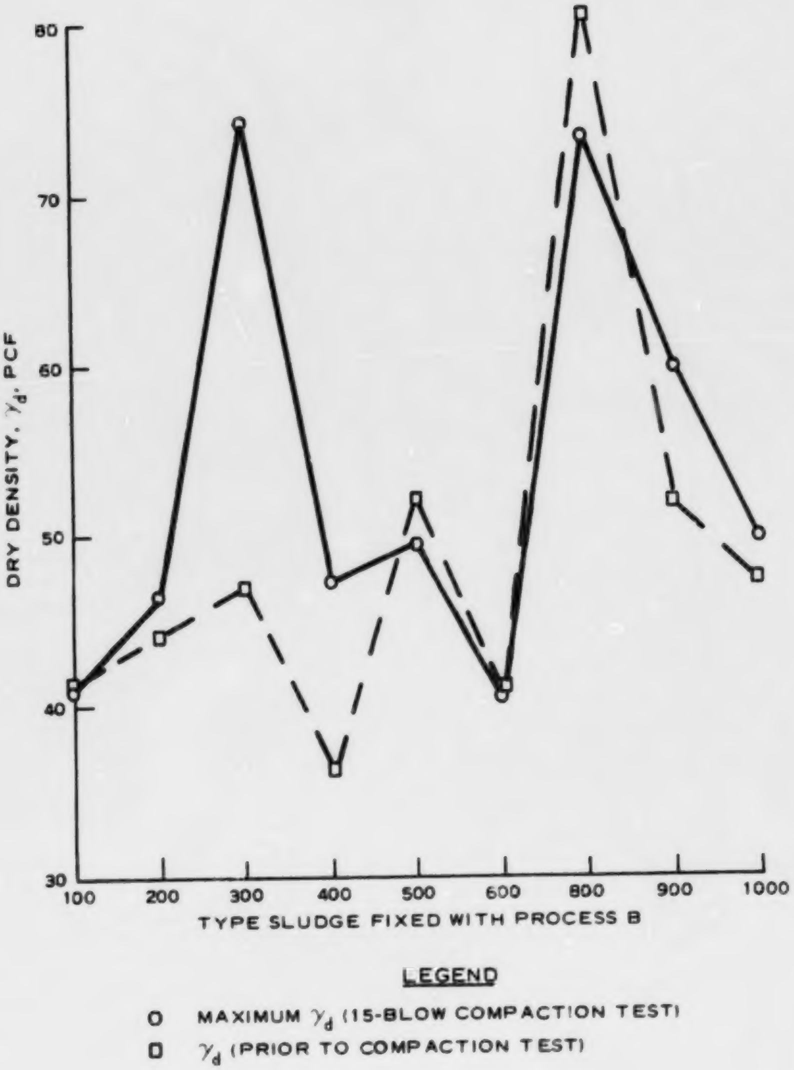


Figure 18. Densities of materials fixed by process B, before and after compaction.

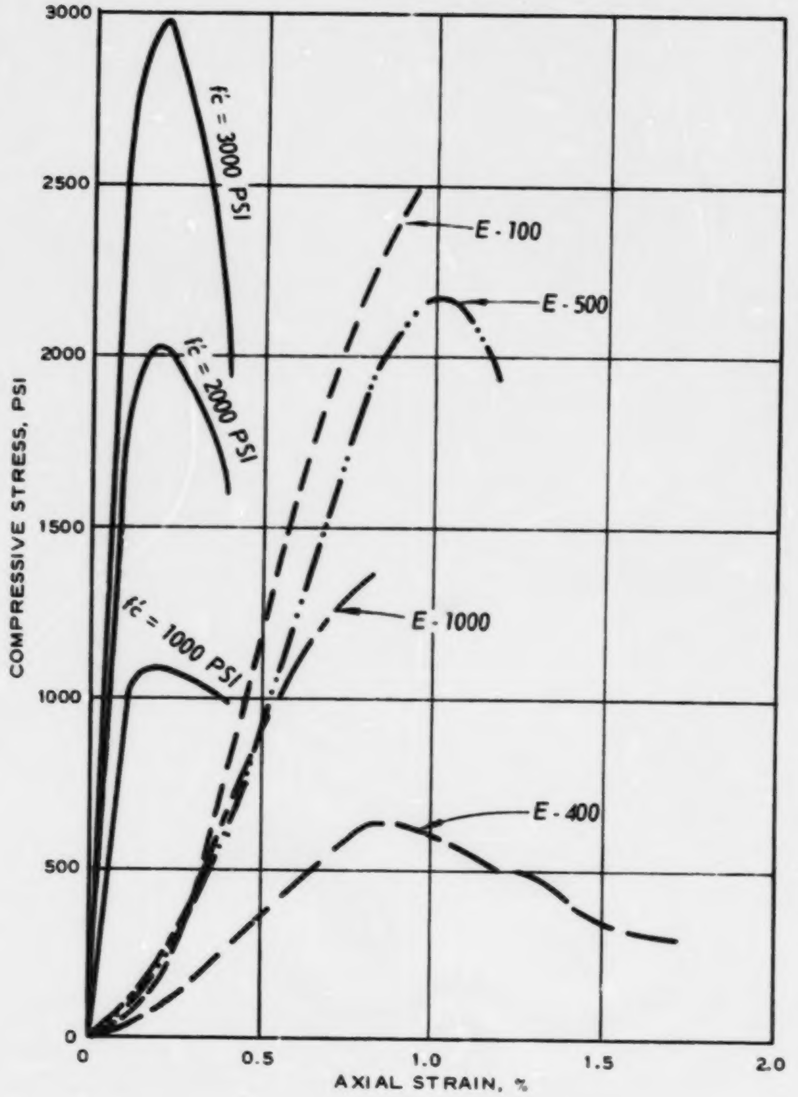


Figure 19. Unconfined compression test, comparison of sludges fixed by process E with concrete. Notes: 1. Solid Lines Are Typical Stress-Strain Curves for Concrete of Compressive Strength Shown. 2. Each Sludge Curve Is Average of 3 Specimens. 3. Compressive Strength of Concrete Determined After 28 Days of Curing.

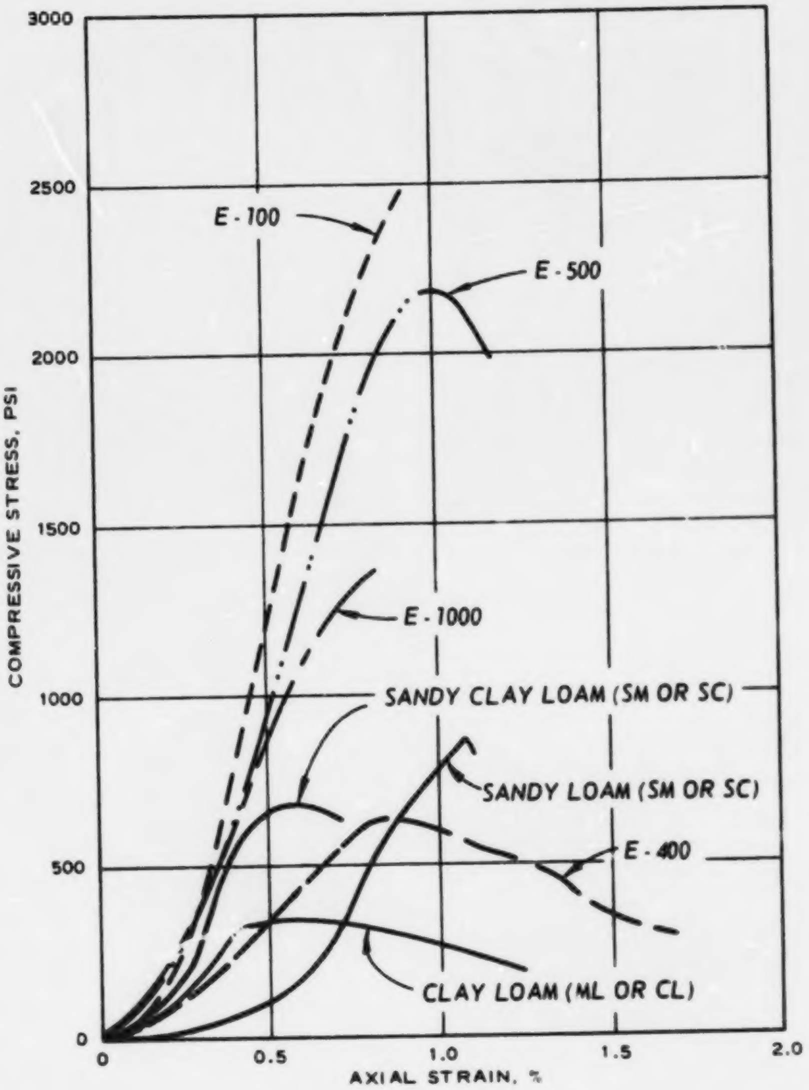
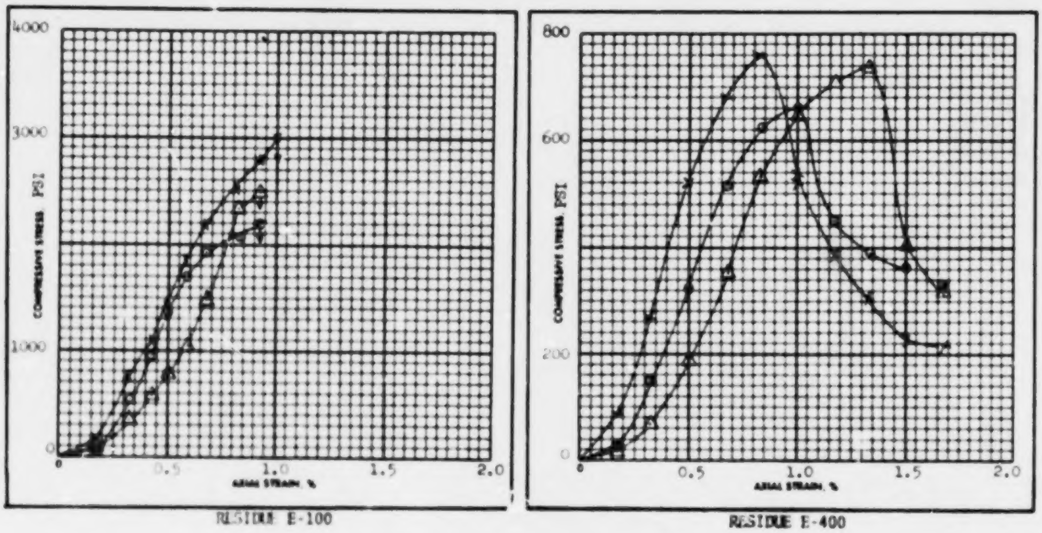
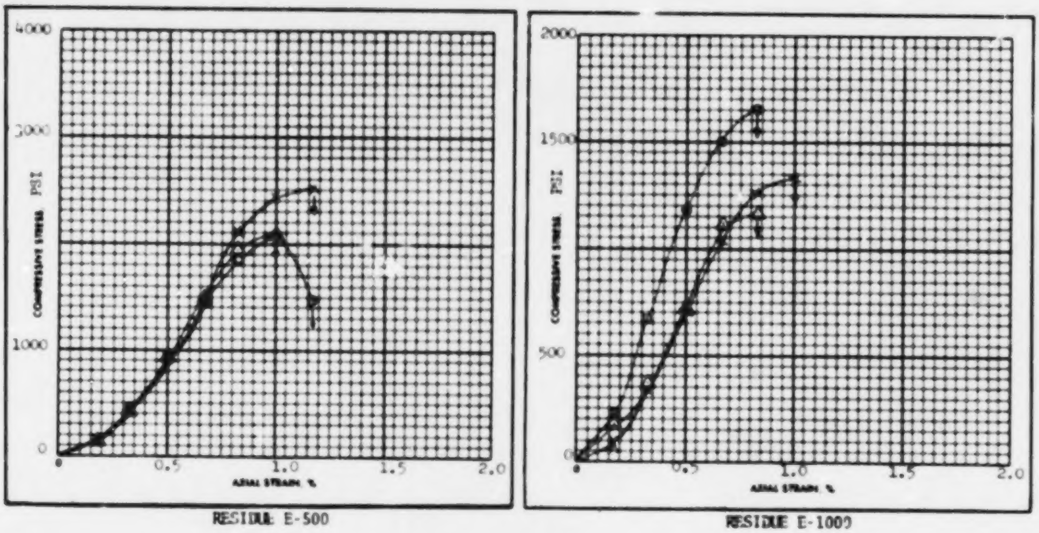


Figure 20. Unconfined compression test, comparison of sludges fixed by process E with soil-cement. Notes: 1. Solid Lines Are Stress-Strain Curves for Soil-Cement Mixtures. Each Curve Is for Type Soil Indicated and 11% Cement Content. 2. Each Sludge Curve Is Average of 3 Specimens. 3. Compressive Strength of Soil-Cement Mixtures Determined After 28 Days of Curing.



RESIDUE E-100

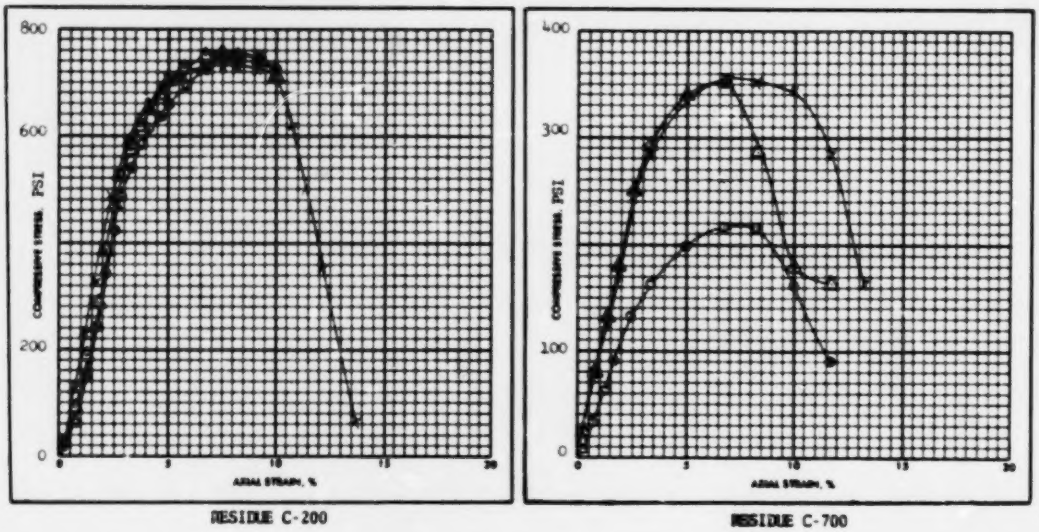
RESIDUE E-400



RESIDUE E-500

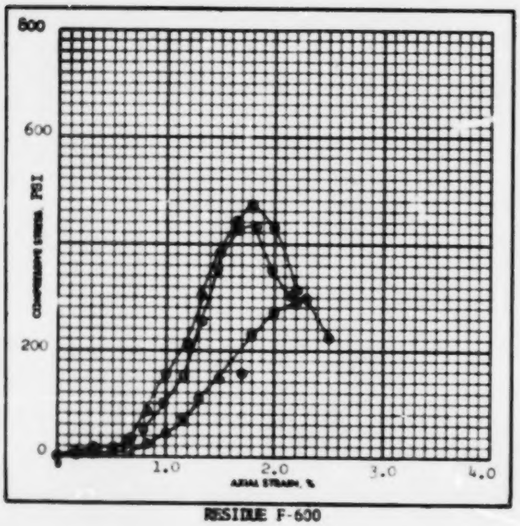
RESIDUE E-1000

Figure 21. Stress-strain curves, fixed sludges (E-100, E-400, E-500, and E-1000).



RESIDUE C-200

RESIDUE C-700



RESIDUE F-600

Figure 22. Stress-strain curves, fixed residues (C-200, C-700, and F-600).

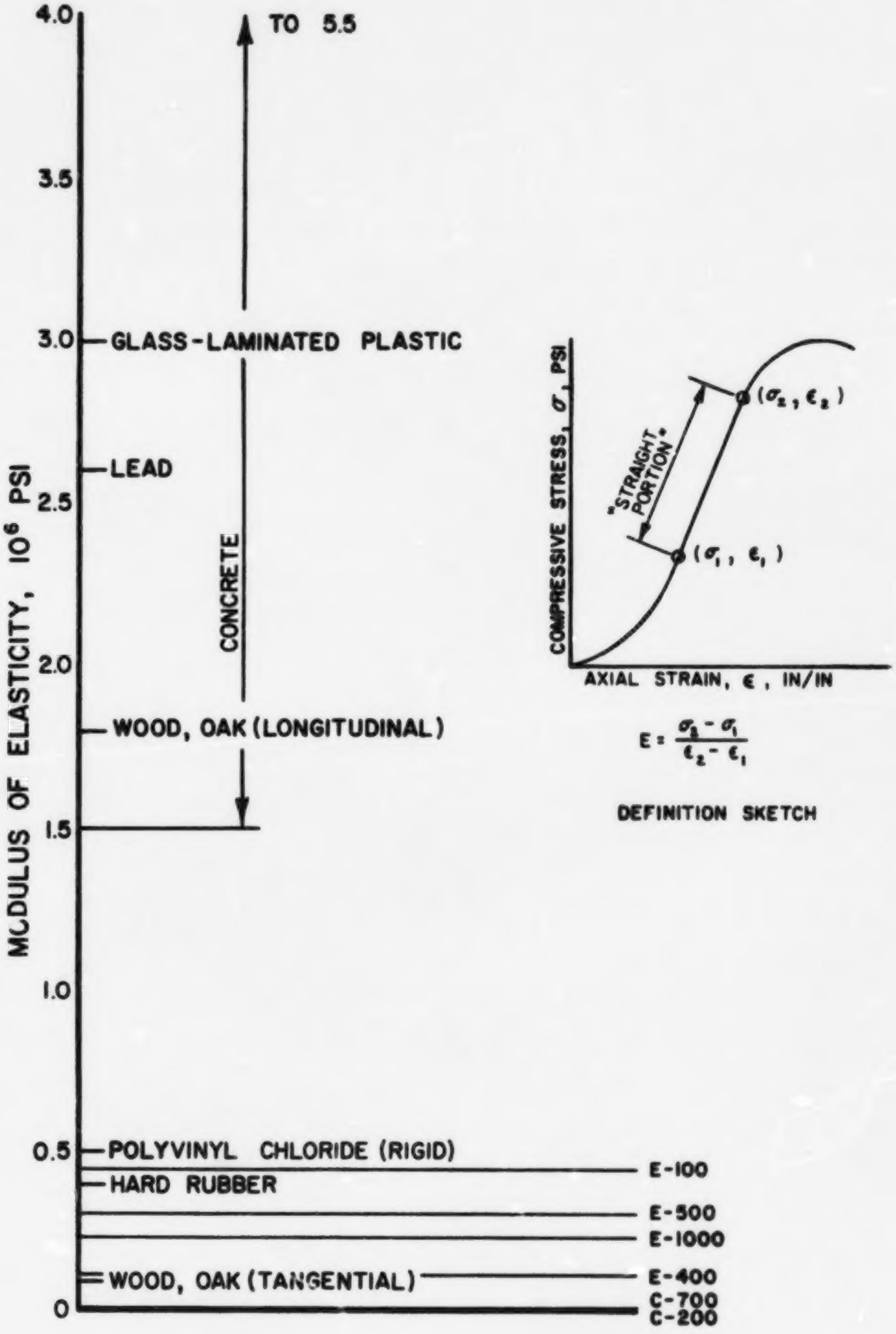


Figure 23. Elasticities of common materials compared with fixed sludges.

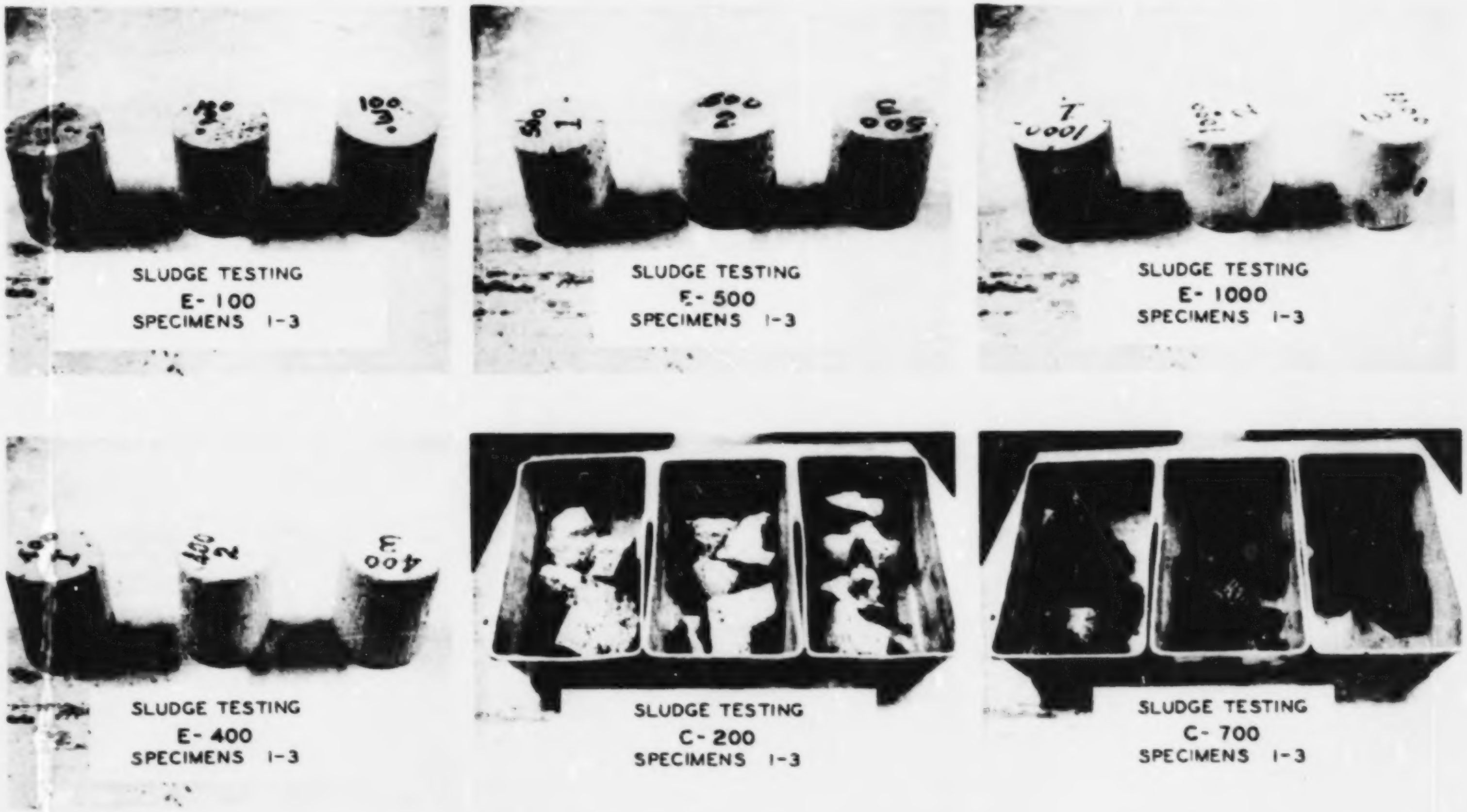

SLUDGE TESTING
E- 100
SPECIMENS 1-3
SLUDGE TESTING
E- 500
SPECIMENS 1-3
SLUDGE TESTING
E- 1000
SPECIMENS 1-3
SLUDGE TESTING
E- 400
SPECIMENS 1-3
SLUDGE TESTING
C- 200
SPECIMENS 1-3
SLUDGE TESTING
C- 700
SPECIMENS 1-3

Figure 24. Results of wet-dry-brush test, processes E and C, 4 cycles

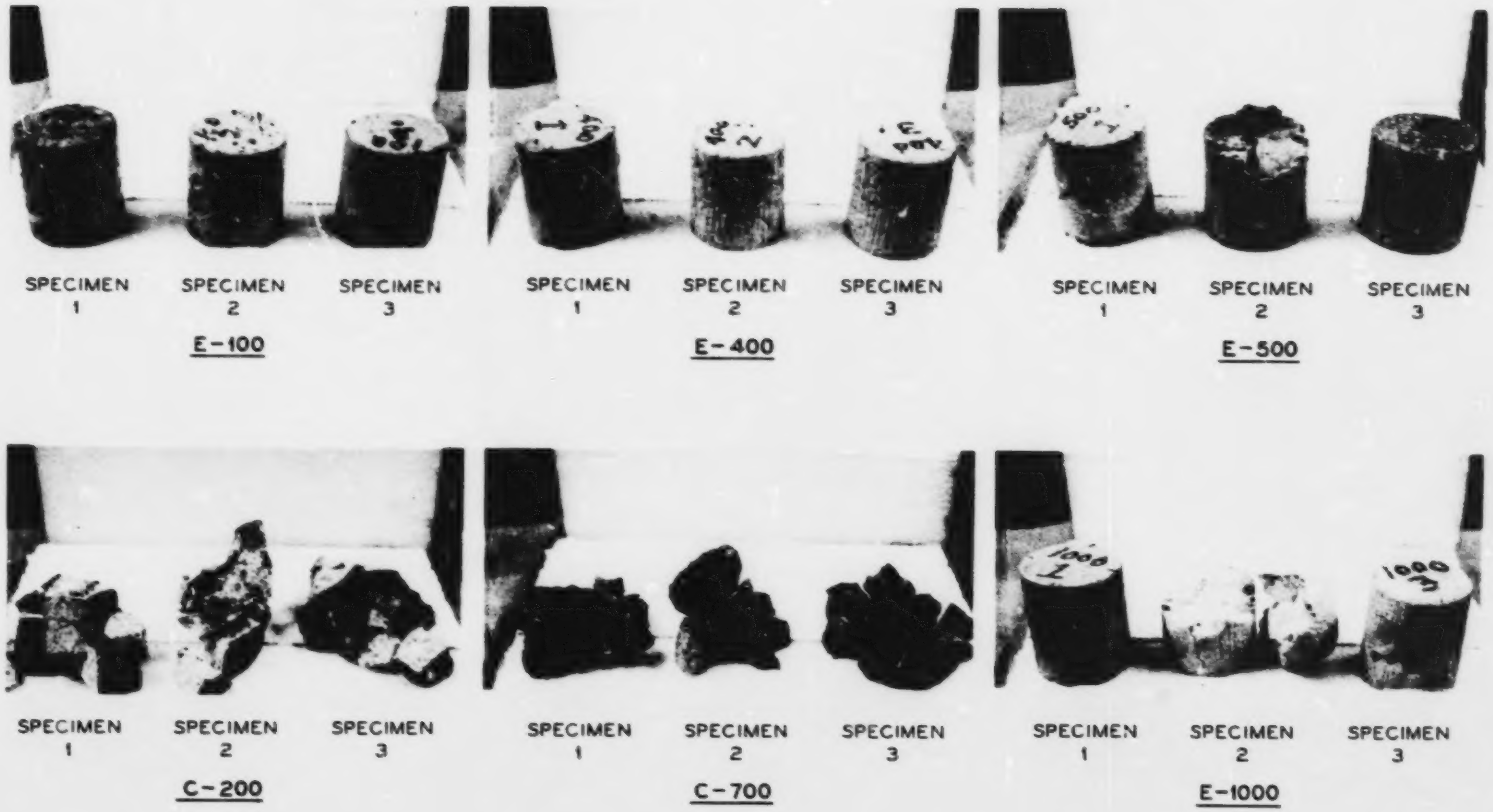

SPECIMEN 1
SPECIMEN 2
SPECIMEN 3
E-100
SPECIMEN 1
SPECIMEN 2
SPECIMEN 3
E-400
SPECIMEN 1
SPECIMEN 2
SPECIMEN 3
E-500
SPECIMEN 1
SPECIMEN 2
SPECIMEN 3
C-200
SPECIMEN 1
SPECIMEN 2
SPECIMEN 3
C-700
SPECIMEN 1
SPECIMEN 2
SPECIMEN 3
E-1000

Figure 25. Results of wet-dry-brush test, processes E and C, 12 cycles

## PRODUCTIVE UTILIZATION OF FIXED SLUDGES

On the basis of the currently available data, speculation may be made regarding the productive usage of fixed sludges. The possibility of productive use of fixed sludges is of merit since it would offset treatment costs. The sludges treated with process B may find use as sanitary landfill cover and in other landfill applications, though shrinkage, swelling, cracking and erosion may be problem areas on the basis of data presented herein. Sludges fixed by processes C and E become quite hard, and this may lead to their utilization as a substitute for low strength concrete. Such substitution might include using these fixed sludges as roadway base courses, runway and taxiway aprons and shoulders, or molding into useful shapes such as bricks, blocks, or drain tiles.

# SECTION VI

# CHEMICAL PROPERTIES

## GENERAL COLUMN BEHAVIOR OF SAMPLES

Chemical properties are being investigated through the use of leaching columns which has been described earlier.[3] The leaching columns are constructed of translucent plastic which allows routine observation of the samples during the leaching period. During the current study period, certain physical changes in sample behavior within the leaching columns have been observed. The purpose of this subsection is to relate these observations to possible chemical and/or physical properties of the raw or fixed residues.

### Leaching Solution

The rate of fluid application to the leaching columns is controlled to an approximate fluid velocity range of $10^{-5}$ to $10^{-6}$ cm/sec. This control has generally been achieved for all samples of fixed residues, due to flow patterns established for these leaching columns. The control of permeability for the raw sludges columns has been more difficult since their permeabilities are a function of the residue category and not control methods. For some of the residues (e.g. 200 and 300), the permeabilities appear to be extremely low which resulted in difficulties in collecting adequate sample volumes for analysis. Permeabilities of the raw sludges will be determined by independent testing to obtain comparative values for all residue categories. The obvious implication to environmental impact is that residues which possess low permeabilities will produce low volumes of leachate. Depending on the concentrations of pollutants in the leachates and quantities of sludge disposed, a low volume of leachate production suggests that ponding may be an environmentally suitable disposal method. Permeabilities of the fixed specimens are lower than the raw sludges; consequently, the laboratory design for leach testing reflected this fact. The use of a system in which the fixed specimens are surrounded by a more porous medium is similar to what would be expected under field conditions. The fixed residue would be exposed to less water in the field than an equivalent amount of raw sludge because of a reduced permeability and surface area exposed.

Permeability also has a bearing on the performance of specimens in leaching columns if pollutant mobility is motivated primarily by a diffusion mechanism.[4] For a diffusion mechanism, a high leach solution flow will produce a maximum leaching in terms of mass of pollutant per unit time;

whereas a low leach solution flow (or static test) results in a maximum concentration of a pollutant per unit time. Thus, the choice of a continuous versus static leach test is made on the basis of which bound (maximum) controls. Each of these alternatives has an associated environmental impact, but for toxic pollutants the latter condition would prevail in most cases. In this study the fluid velocity for the leaching has been adjusted to the minimum rate feasible under present limitations of the experimental facilities. Due to limitations of the hardware, it was difficult to regulate fluid velocity of the leaching solutions precisely. The volume of sample collected is measured and velocities may be calculated assuming constant flow during the sampling period. Spot checks of leach fluid velocities for the facility have demonstrated variations between columns. The effect of these variations upon leachate quality has not been determined; it, however, is probably minimal for the range of rate used in this study.

## Physical Characteristics

During the period covered in the report, several physical alterations were noted for certain specimens in the leaching columns. Generally, there have been color changes exhibited by some of the raw sludge samples. The degree of color change is inconsistent between replicates and usually is evident only in the top few centimeters of the solids. At this time, it is unknown whether these qualitative changes are a function of chemical or biological actions. The former is more suspect because most of the residues currently tested lack sufficient organic carbon to support biological growth. Additionally, most residues contain chemical constituents that would be detrimental to most microorganisms. The effect of these subtle quality changes are probably not of the extent that could be quantitated by the present analytical program.

The specimens for residue 400 fixed by process B demonstrated an obvious physical deterioration during the leach testing. Process B results in a product with a coarse particle distribution resembling a soil-like material. The deterioration for these specimens was manifested by a gradual consolidation of the particles into a gelatinous mass. This physical change was almost complete at the end of 90 days exposure in the leaching column and was uniform for all replicates. This obvious physical change was equated to process failure for this residue; consequently, this particular residue was reprocessed and the testing program initiated again. Reprocessing was accomplished by adjusting the additives/residue ratio and appears to have been successful.

Specimens for residue 400 fixed by process E demonstrated a swelling reaction upon exposure to the leaching solutions. Specimens fixed by process E are molded into cylindrical shapes for testing. In this case the swelling was so severe that the leaching column was ruptured. The swell reaction was assumed to be complete at this point and the specimens were loaded into new columns and testing continued; no additional swell reaction has been observed. The swelling reaction has not been observed for other processes. This particular reaction is being investigated in detail to determine its possible implications to engineering properties.

The physical changes noted during the present testing program have been documented for their possible effect on process performance. Ultimately, this information should be related to quantitative data available from leach testing to ascertain performance effects. Some of these physical changes are probably related to process control for fixation of specific samples; therefore, they may not necessarily reflect on optimum process performance. Conversely, some physical changes may be related to testing procedures and these would be significant in interpreting process performance.

## CHEMICAL PROPERTIES

### General Chemical Characteristics

The chemical properties of the raw and fixed sludges were investigated by leaching columns. The chemical properties of leachates discussed within this report include pH, conductivity, sulfate, and copper. These parameters were selected as being representative of the leaching data available. Two leaching solutions were used and all specimens were tested in triplicate. Column assignments were made at random throughout the system and control (blank) columns were included. Replication allows determination of the error for a given sample, while inclusion of blanks allows establishment of background noise for the analytical tests and assessment of general system reliability.

Data for the blank columns have been included within the specific results presented in this section but are summarized for the pH 4.7 leaching solution in Table 15. This data demonstrates that background levels for the parameters discussed are very low. These results are reported as the means for the replicate control columns. Data from the control columns may be utilized in two ways. First, since it represents background for the chemical properties, it may be used to establish whether leach rates are significantly different from those of the control columns. For the data from columns containing fixed samples, this is particularly important to determine whether leaching of a given chemical is actually occurring. Second, the control columns are assigned randomly throughout the system; therefore, low levels for analyzed parameters indicate high system reliability (i.e., no feeder line leaks or crossflow). For the chemical properties included in this report, the system reliability is high.

Volumetric leach rates (leach solution fluid velocity) for the columns are important for assessing mass leach rates (mass of pollutant leached per unit time). In most cases the volumetric leach rates for the raw residues are lower than those for the fixed residues. This means that interpretation of leach data on the basis of pollutant concentration (equal leachate concentrations for raw and fixed specimens) indicates mass leach rates for fixed specimens are higher, implying that presentation of leach data in terms of concentration is conservative for the fixed samples. Comparison of raw and fixed sludges in a field disposal operation by the above manner must also consider the relationship to the natural event producing the leachate. If rainfall or water influx into the disposal area produces leachate, the volumes produced from fixed residues may be smaller than those produced from raw sludges because of reduced permeability and the geometric scale factor between laboratory and field situations. For small volumes of fixed sludge, the control will lie in the permeability of the material surrounding the sludge, but for large volumes (or areas) control will lie with the permeability of the fixed residue. In summary, for laboratory studies mass leach rates may conceivably be higher for fixed sludges than raw sludges, but interpretation of these results in terms of environmental impact in the field must consider differences in the physical configurations of these two systems. An advantage of presenting data in terms of mass leach rates is that the problem of variable volumetric leach rates is eliminated. Presentation of concentration gives more readily understandable data, especially in terms of potential environmental impact, and this method will be used preferentially in this report.

Table 15. CHEMICAL PROPERTIES OF CONTROL COLUMNS

| Parameter | Mean Value |
|---|---|
| pH | 5.6 units |
| Conductivity | 97 umhos/cm |
| Sulfate | 8.0 mg/l |
| Copper | 6.6 μg/ℓ |

A critical problem in understanding potential environmental impact of residue disposal is the chemical and physical form of the material being leached. This is particularly true for the metals which may be transported as soluble, complexed, or colloidal species. The philosophy behind the present study is to assess pollutant movement from a disposal site containing either raw or fixed sludges. The disposal site is defined as that region containing the residue and excluding all surrounding areas. In this case, it is feasible that a majority of the pollutants leached from the columns are not in the soluble form. This fact may be confirmed by noting that the solubilities for some metals in an alkaline pH are far below the detection limits of analytical procedures employed.

For the copper data presented in this report this means that most of the metal is being transported in the complexed or colloidal state. The environmental impact of these species is not well defined; consequently, the overall impact of these leaching tests may only be indirectly determined. Additionally, since most of the specimens exhibit complex chemical properties, antagonistic and synergistic effects must be addressed.

## Descriptive Parameters

The descriptive parameters included in the chemical properties are pH and conductivity. The pH of the leaching solution is directly related to the solubility of the metal pollutants and conductivity is proportional to the dissolved solids present in the leachate. These parameters were measured to give an overview of the chemical status with respect to the leachates.

An analysis of these parameters by residue category should result in partial understanding of the basic behavior for the system.

pH-Plots of pH by sludge category for raw and fixed specimens are presented in Figure 26. These plots are based on mean values for all leachate replicates, over the present sampling period, from the pH 4.7 buffered leach solution. The plots are intended to present a spatial representation of pH for comparative purposes between all samples.

The displacements with respect to the raw sludge location on a given plot are consistent for all but one residue category. An ordered arrangement can be made between processes relating this displacement to increasing pH. This ordering with respect to pH results in B > E > F > A > D > C for the respective processes. An exception to this ordering occurs for sludge 500 where E > B > A; in this case the locations for E and B are nearly equal, Figure 26.

The relative position of the raw sludges with respect to the above ordering is related to the pH of the raw residues. Those residues characterized by a high pH (> 12), result in an ordering of R > B > E > F > A > D > C. All remaining residues result in an ordering B > E > F > A > R > D > C. Because the ordering is consistent between all sludges, it would tend to imply that the effect of the processes is consistent between all residues. The concept would tend to greatly simplify evaluation of fixation processes for different types of residues.

For all residues except 300 and 500 the latter ordering presented above may also be related to fixation methodology. Processes B, E, F, and A essentially utilize inorganic additives and lie above the position for the raw residue, R. Process D, an encapsulation process, and process C, which utilizes an organic additive, both lie below the position for the raw residue, R. Generally, one effect of fixation processes utilizing inorganic additives seems to be elevation of pH. The relationship of process D with respect to ordering probably does not relate to a specific effect on leachates since it is an encapsulation process. The relationship for process C to ordering cannot be related specifically to an organic process.

The above data implies that a predominant effect on leachate solutions by fixation may lie with pH changes. This concept should be related to observed pollutant mobility, particularly for the metals which are less mobile at a high pH due to formation of insoluble hydroxides. The effect of fixation upon leachates is more complex than stated above, but the pH effect is one which can be documented by observed data.

Stability of pH Measurements-If the concept of fixation motivated pH changes on leachate behavior is accepted, the stability of these effects should be documented. The stability of these effects is important because of potential implications on disposal and longevity of the fixation process. An example of the pH stability exhibited by one of the fixation processes is presented in Figure 27. It can be observed that the pH of the raw residue is fairly stable with respect to time. In contrast the pH of the fixed residue is initially distinct from the raw residue but the curve is converging with raw residue. This behavior is obviously related to elution

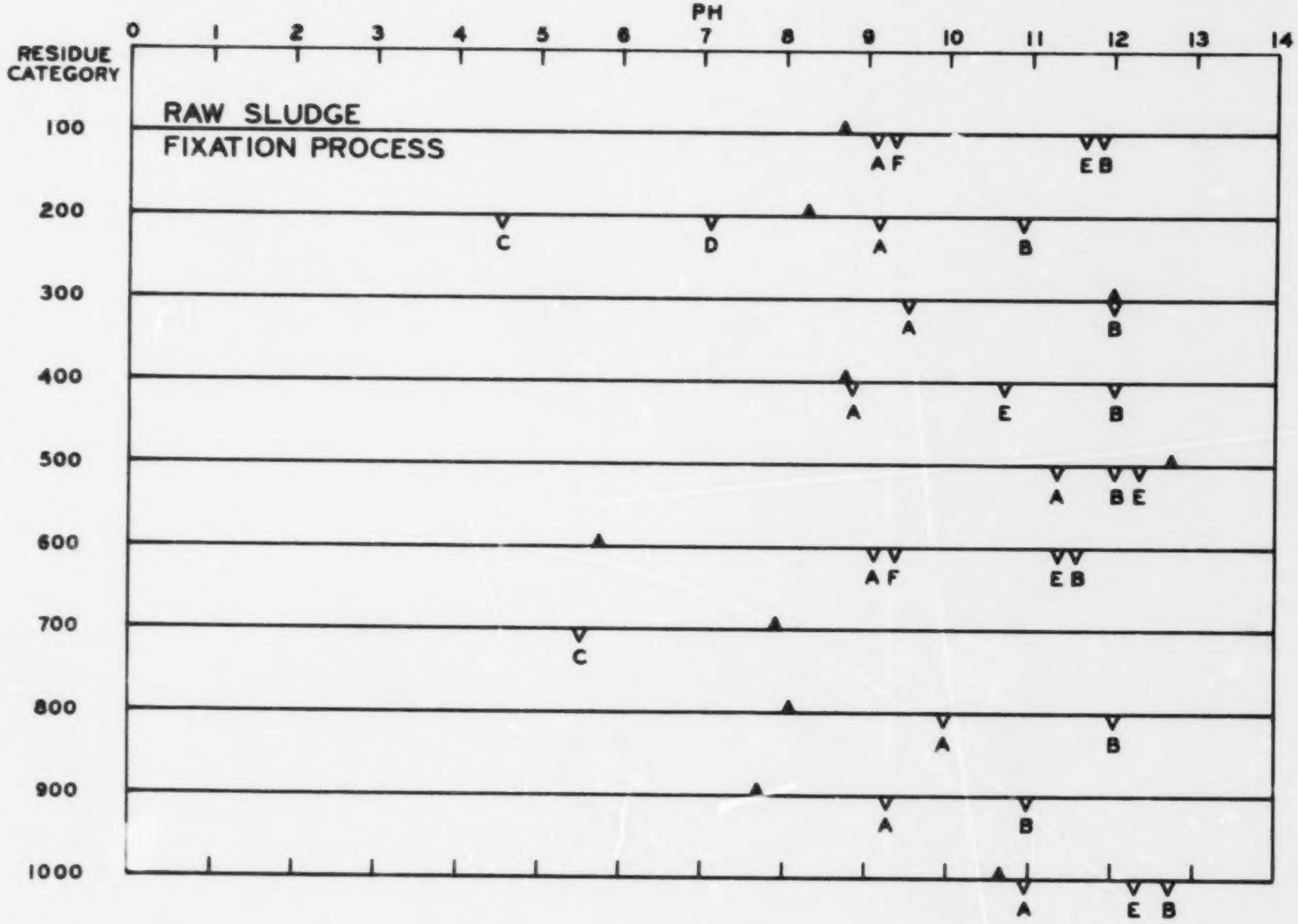


Figure 26. Leachate pH for raw and fixed residues.

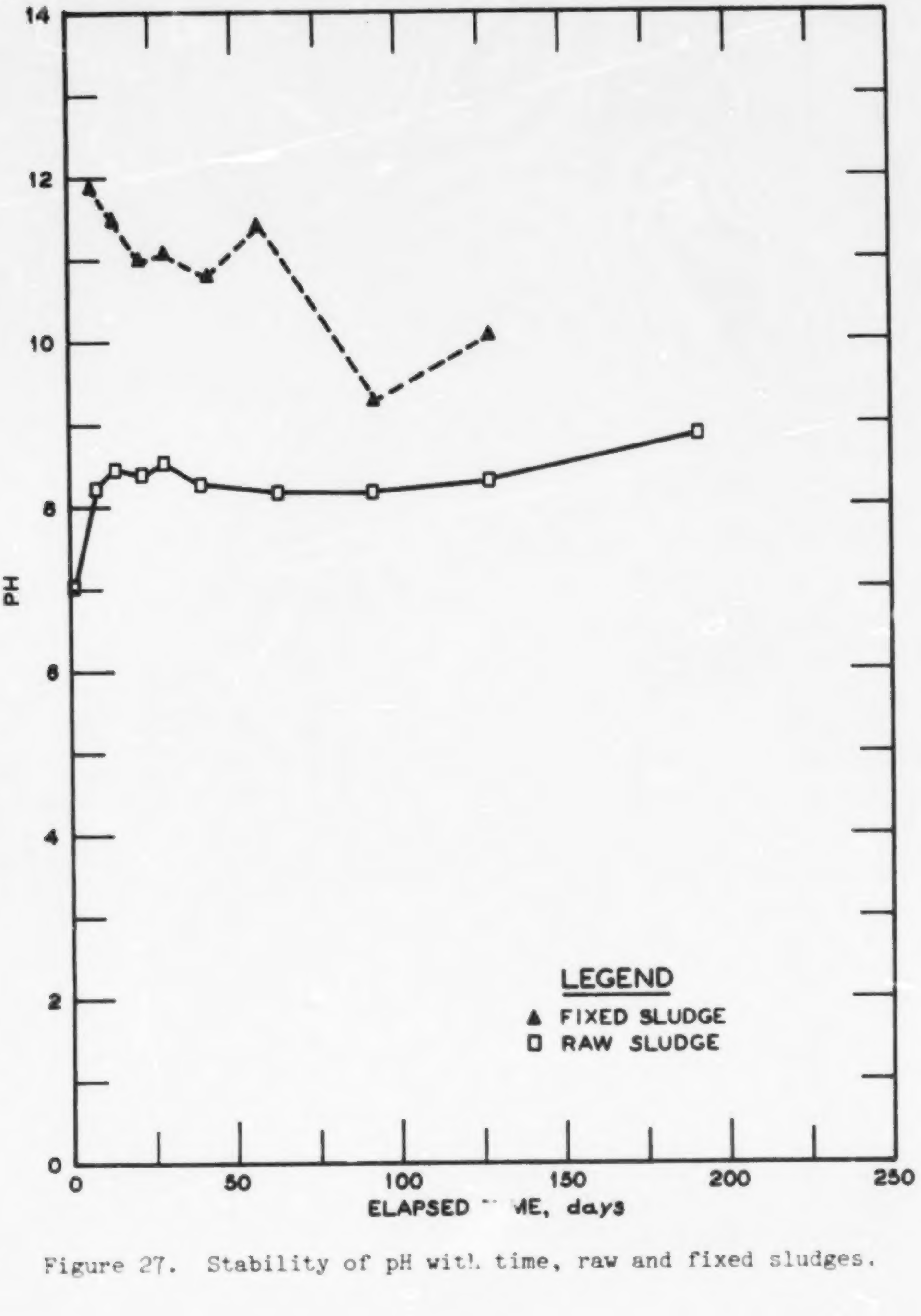


Figure 27. Stability of pH with time, raw and fixed sludges.

and the volume of leaching solution applied. These data have been observed for other specimens, but do not necessarily reflect the behavior of all systems tested to date.

If the convergence of the pH curves, Figure 27, represents realistic behavior for the leaching systems, then there exists some time at which the pH for the raw and fixed residues will be similar. At this point the leach behavior of the two systems should be similar if the pH effect predominates for a given fixation process. Observance of this type of behavior can be related to quantities of leach solution applied and a calculation of the time for convergence may be made. If the pH effect is not predominant, then this behavior will not be observed.

Conductivity-The conductivity of the leachate is a function of the dissolved solids present and is presented by residue in Figures 28-37, respectively. The data presented are the means for all replicates of the pH 4.7 leaching solution. The conductivities for the raw sludges appear to be highly variable as a function of time, but the trends are either stable, (residues 100, 200, 300, 400, 500, and 900) or decreasing (residues 600, 700, 800, and 1000). The conductivities for the fixed residues are also variable, but generally appear to be decreasing with time. The above noted behavior is consistent with theoretical behavior which would predict decreasing conductivity (dissolved solids) in the leachates as a function of time. The rate at which the conductivity decreases is a function of available material for dissolution and the application rate for leaching solutions. Those residue categories exhibiting a stable conductivity as a function of time are characterized by more available solids for dissolution than those residues demonstrating a decreasing conductivity. The rate of conductivity decrease is related to the state of materials with respect to dissolution. Those residue categories which show rapidly decreasing conductivities, residues 800 and 1000 (Figures 35 and 37), possess contaminants which are more soluble than the remaining residues. As a consequence the pollutants are leached from the columns rapidly and the measured conductivities reflect this release rate.

The relationship between conductivities for the raw and fixed specimens for a particular residue are of interest for comparative purposes. In some cases conductivities for the fixed materials are equivalent to conductivities of the raw residues, (e.g., residues 100, 500, 600, 700, 800, and 900). This indicates that fixation does not substantially affect the conductivities of the leachates. In other cases, (e.g., residues 200 and 300) the conductivities are improved by fixation. In the case of process D, encapsulation, the conductivity is not significantly different than that of the effluents from the control (blank) columns. The converse of the above represents the third situation (e.g., residues 400 and 1000) where the conductivities of the leach solutions increased as a result of fixation. For residue 400, Figure 31, this would seem to indicate that the additives utilized in fixation were responsible for deterioration in leachate conductivity. This fact may also be responsible for stability of the fixed leachates for the first case through selective retention of some contaminants, but release of compounds associated with the fixation additives. For residue 1000, Figure 37, the leachates from the fixed residues demonstrate a significantly higher conduc-

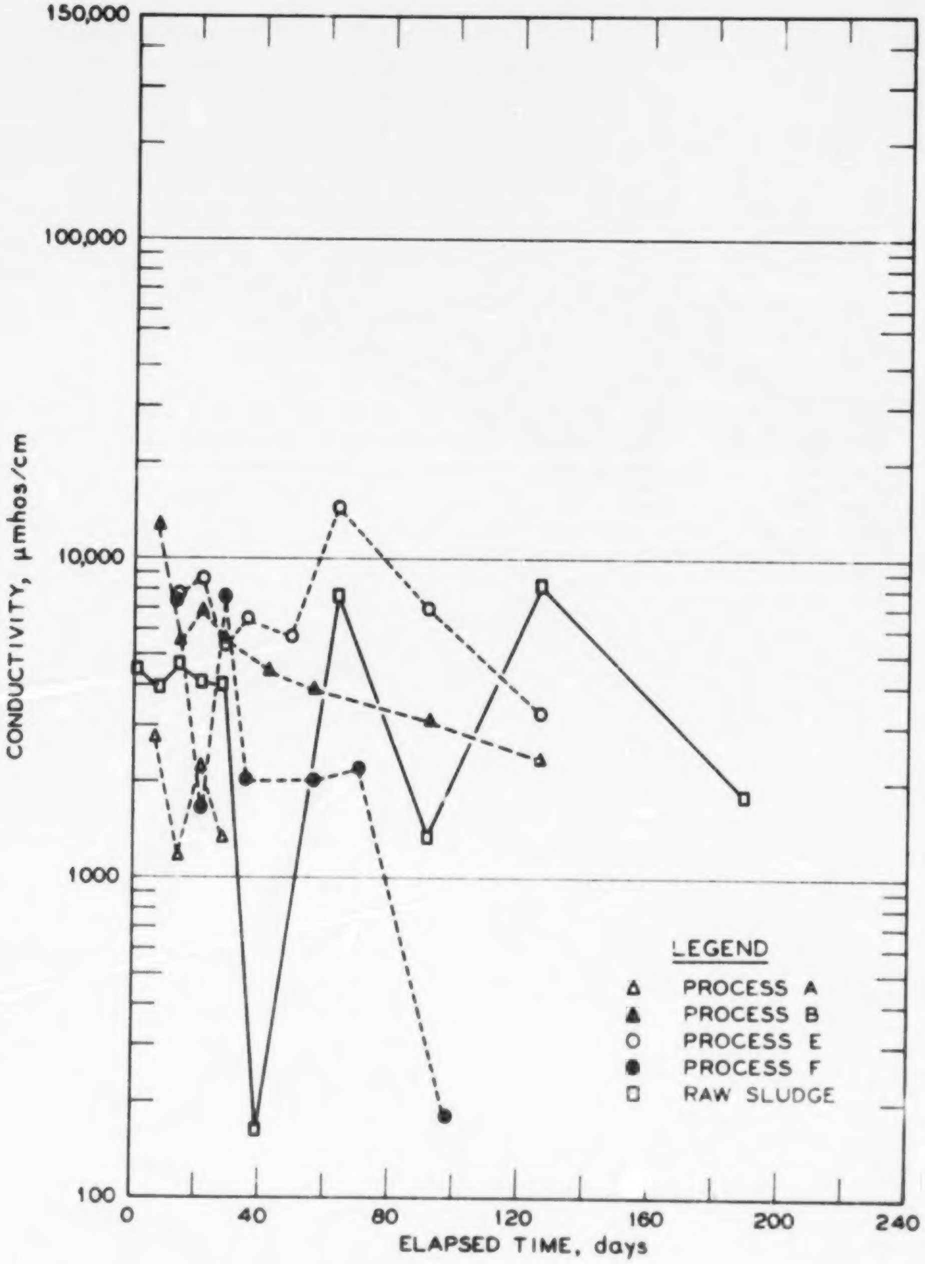


Figure 28. Conductivity versus time, raw and fixed residues: Number 100.

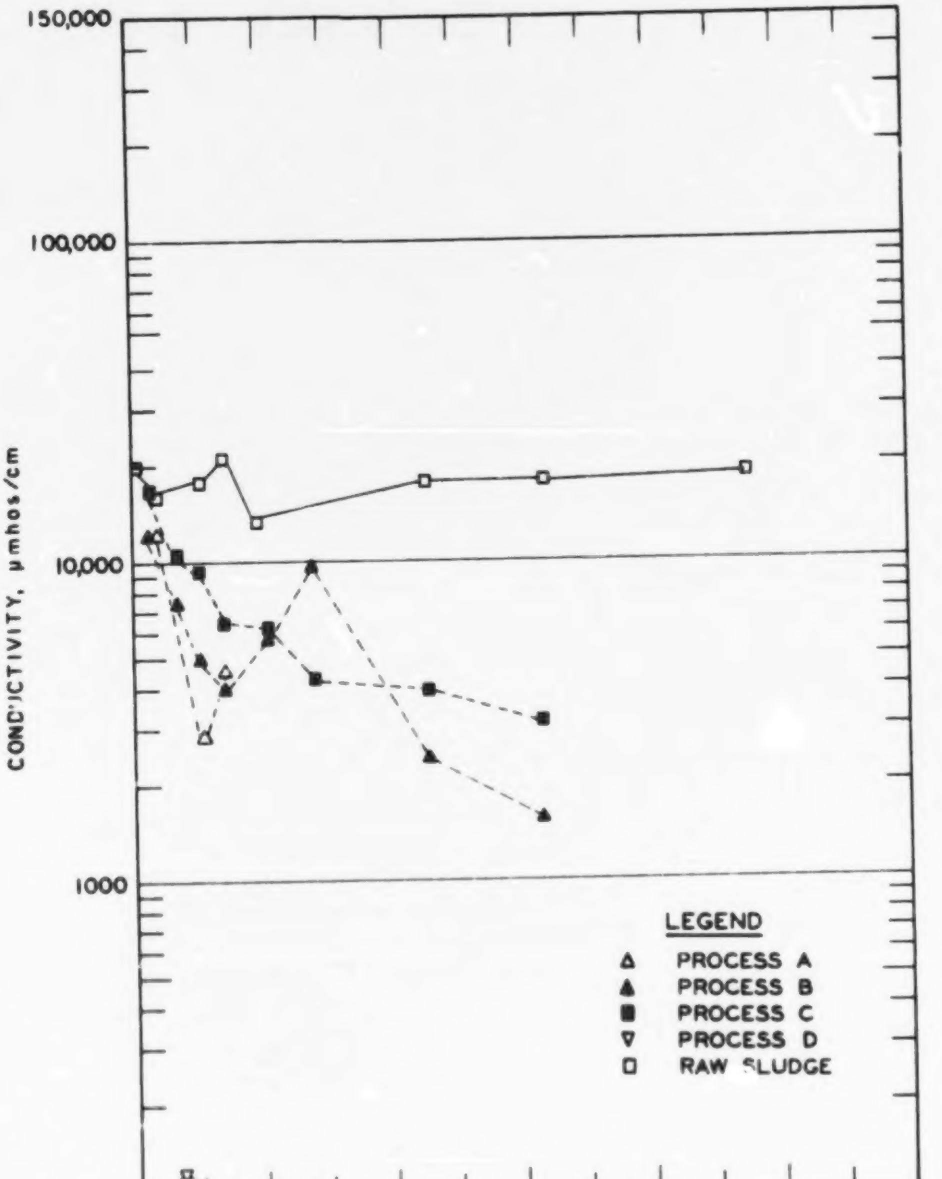


Figure 29. Conductivity versus time, raw and fixed residues: Number 200.

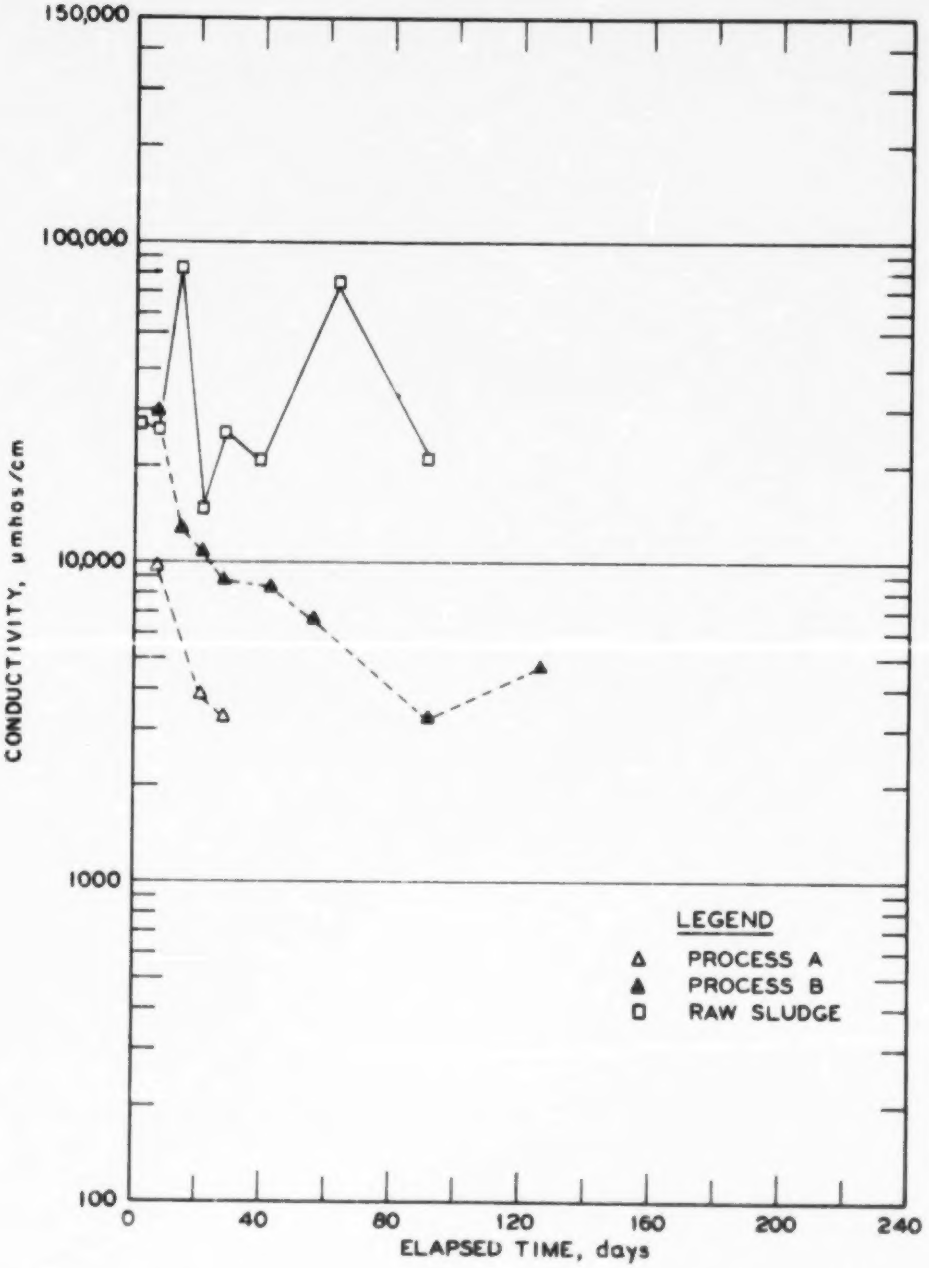


Figure 30. Conductivity versus time, raw and fixed residues: Number 300.

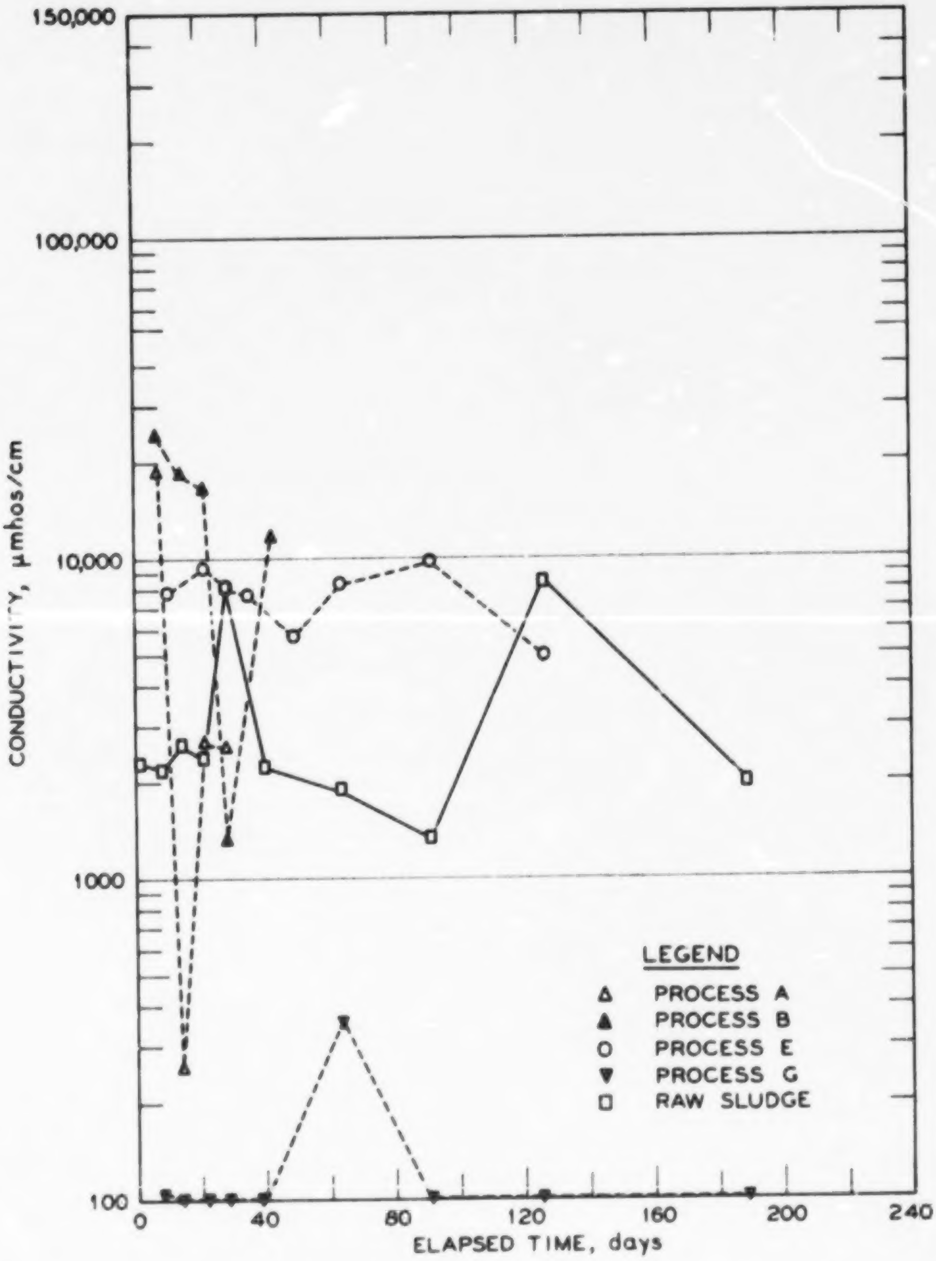


Figure 31. Conductivity versus time, raw and fixed residues: Number 400.

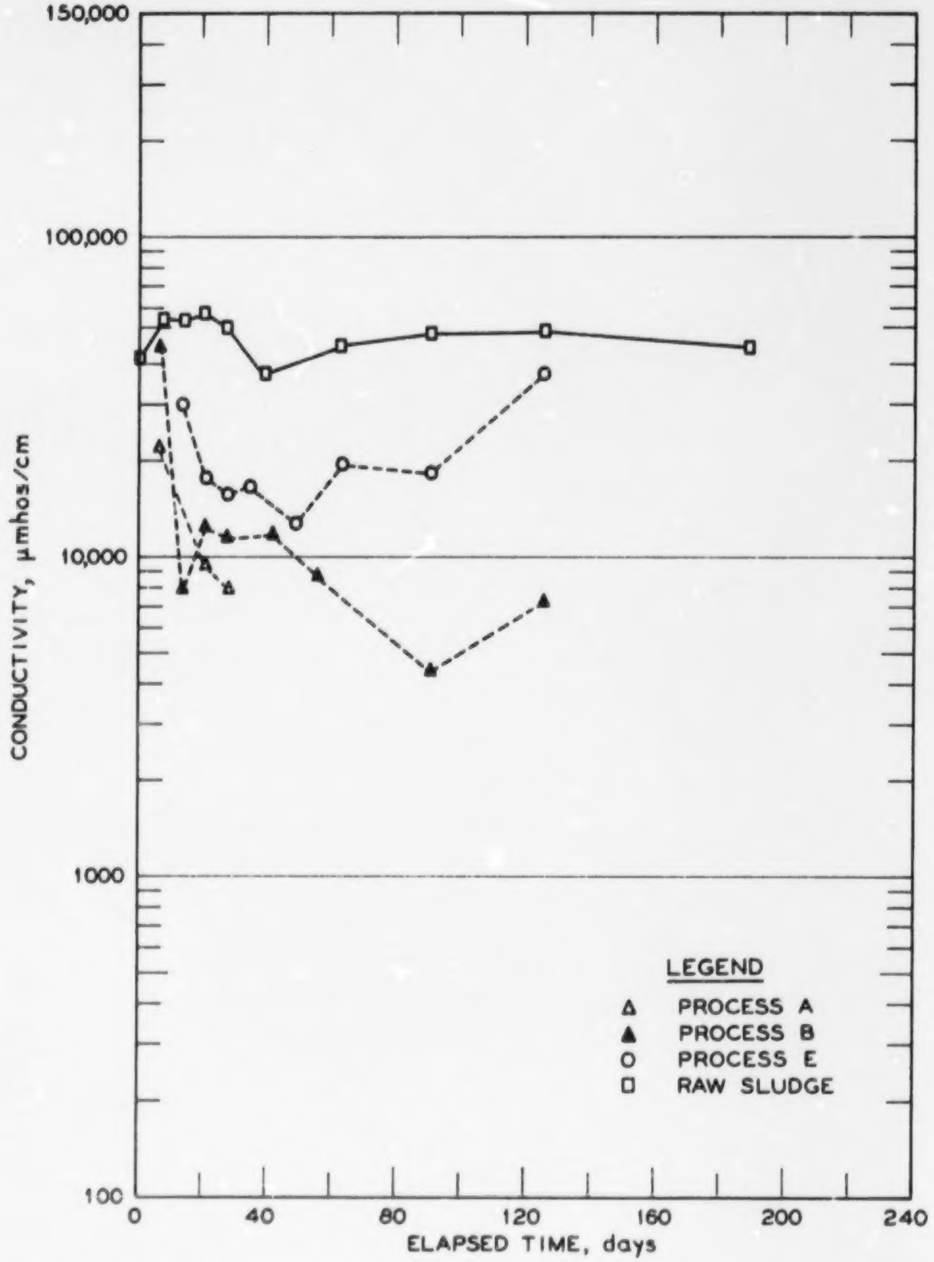


Figure 32. Conductivity versus time, raw and fixed residues: Number 500.

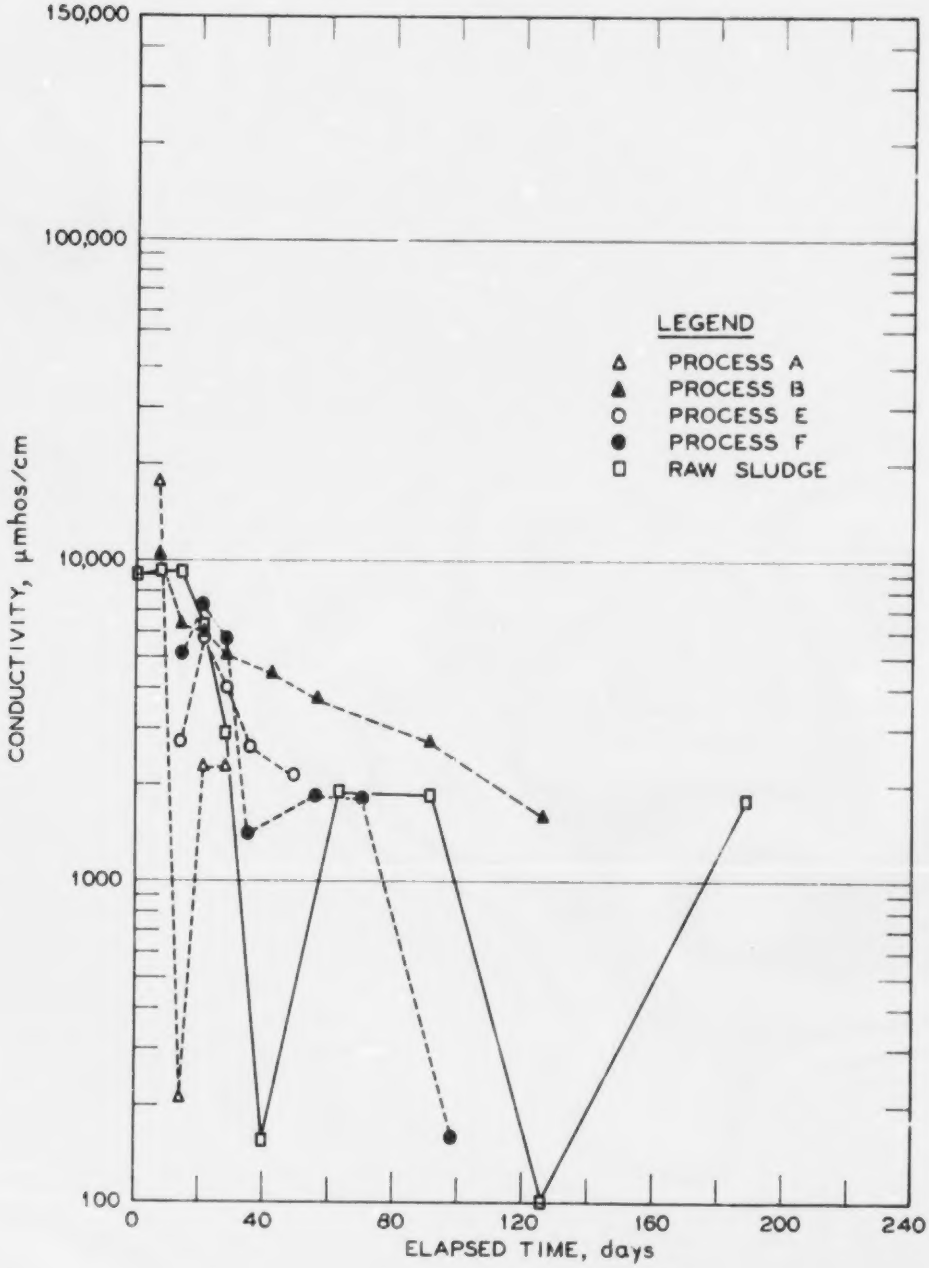


Figure 33. Conductivity versus time, raw and fixed residues: Number 600.

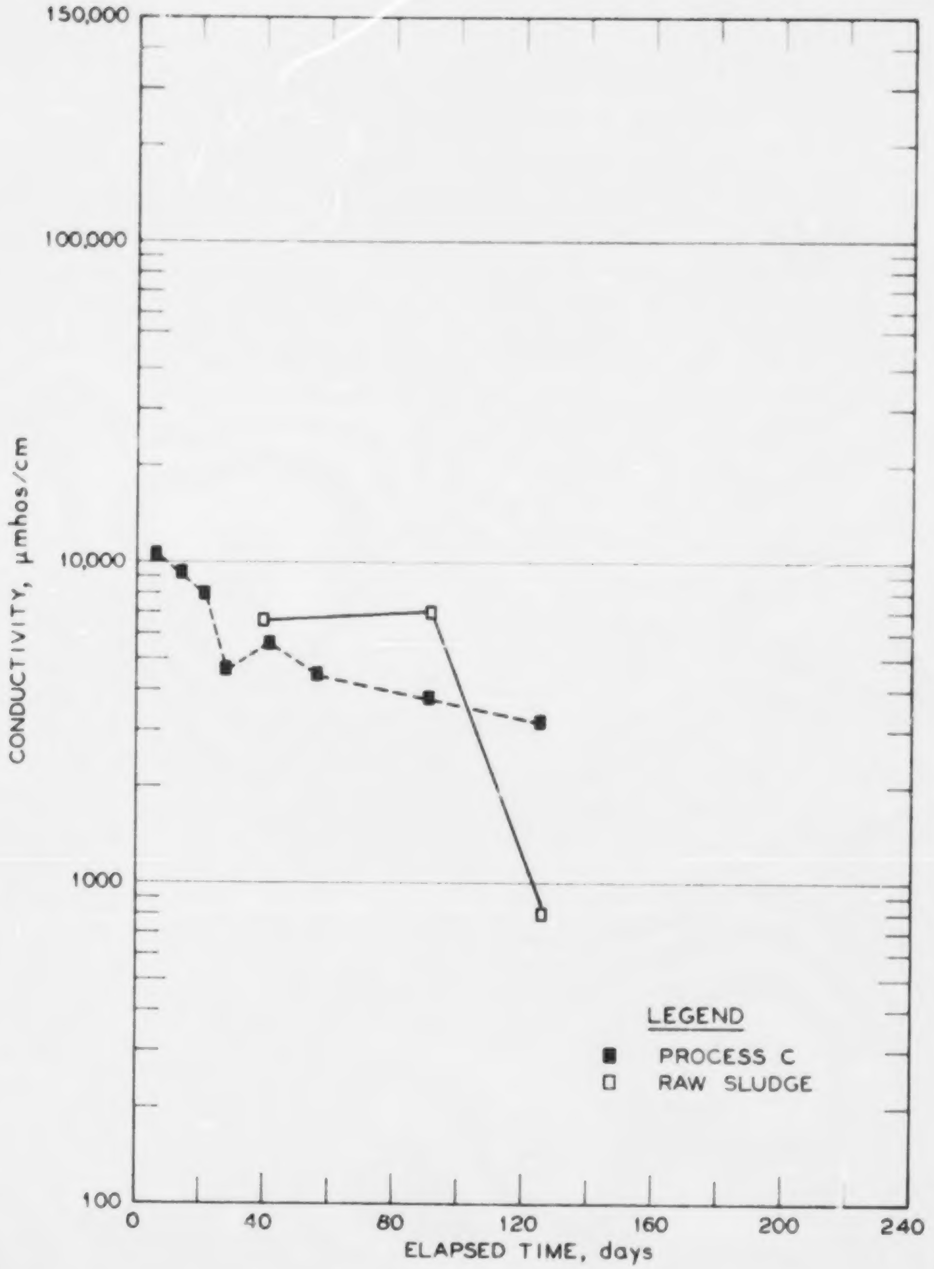


Figure 34. Conductivity versus time, raw and fixed residues: Number 700.

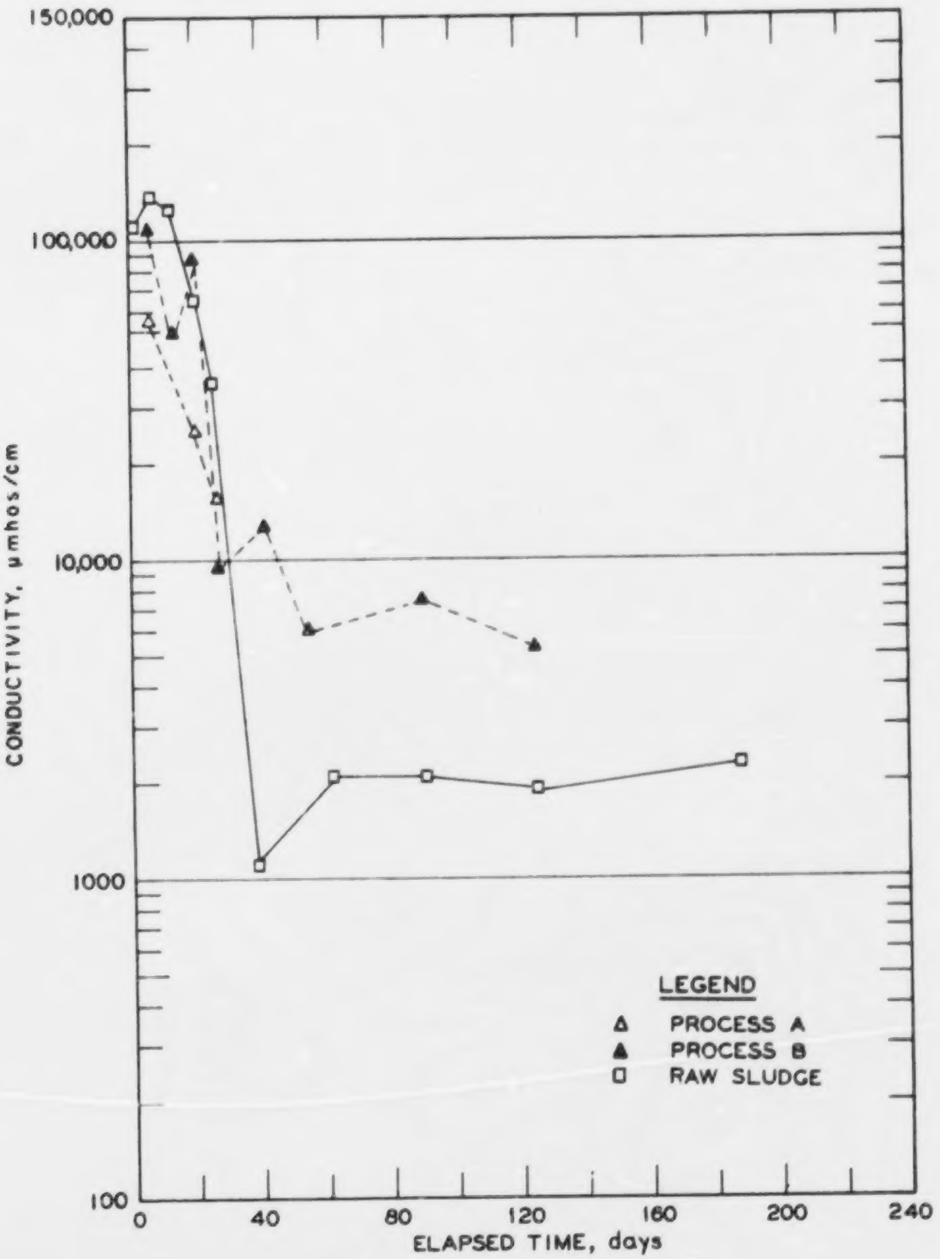


Figure 35. Conductivity versus time, raw and fixed residues: Number 800.

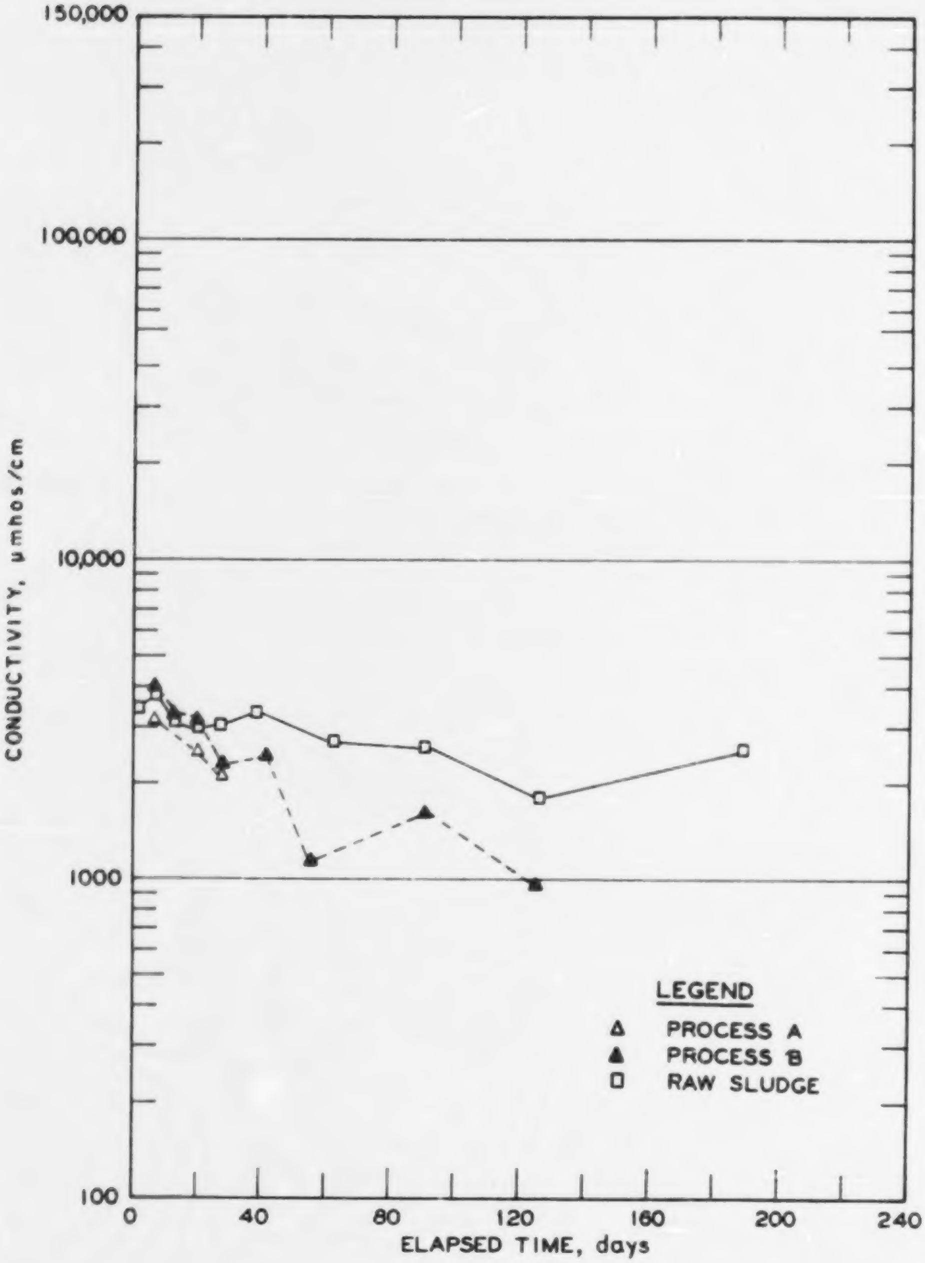


Figure 36. Conductivity versus time, raw and fixed residues: Number 900.

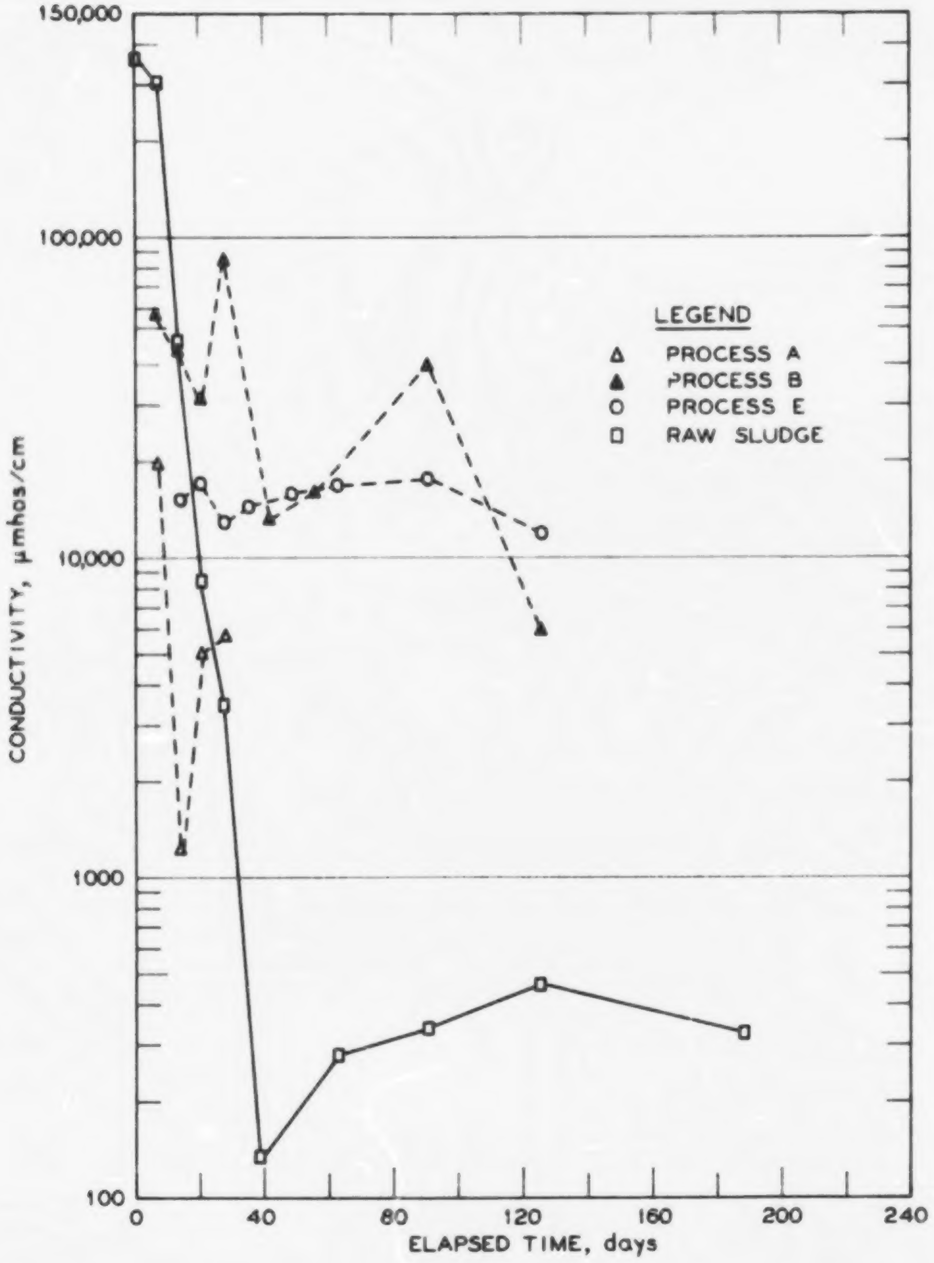


Figure 37. Conductivity versus time, raw and fixed residues: Number 1000.

tivity than the raw leachate after the initial leaching period. This observation may be related to the ability of the fixed residues to retain a certain portion of the readily soluble compounds in the raw sludge, but is subject to a threshold release rate upon leaching. This is a definite advantage for fixation because the environmental impact of leaching at a decreased rate for a particular residue is probably lessened.

Conductivity is proportional to dissolved solids in the leachates, but no quantitative relationship exists for the specimens tested. Conductivity does reflect the general quality of the leachates; consequently, it should be related to the release patterns of other pollutants. The observation that most leachates demonstrated relatively high conductivities indicates that they are leaching dissolved solids and may have an environmental impact.

### Analysis of Descriptive Data

To reinforce the conclusions stated previously and to analyze the effect of experimental design upon leachate behavior, the data from a selected residue, 100, was subjected to an analysis of variance. The design used included all replicates for six time periods, two leaching solutions, and four sludge treatments (one raw and three fixed). This design constituted a repeated measure testing on all these descriptive parameters.[15,16]

The results of analysis of variance for pH are presented in Table 16. The most significant sources of variance are residue, treatment, time, treatment-time interaction, and treatment-leachate-time interaction. These results would tend to confirm the conclusion that there is a definite pH effect upon residue fixation and that this effect is a function of time (pH convergence on sustained leaching). The sources of variance representing leaching solution applied, treatment-solution interaction, and time-solution interaction possess only one significant term. This fact implies that leachate behavior, with respect to pH, is independent of the leaching solutions used in this experiment. Since most of the raw and fixed residues demonstrate a strong buffering capacity, the effect of pH in the leaching solution upon column effluent is small and would support the practice of leach testing with one solution. The difference between the two leaching solutions used in this experiment is not great (e.g., pH 4.7 vs. pH 7.7); therefore, these effects may become significant if leaching solutions of extreme pH ranges were utilized.

Table 16. ANALYSIS OF VARIANCE FOR pHL Residue 100

| Source | Sum of squares | Sum of freedom | F[a] |
|---|---|---|---|
| Residue treatment(s) | 242.1 | 3 | 28.35*** |
| Leaching solution(L) | 14.3 | 1 | 5.00* |
| Time(T) | 12.1 | 5 | 6.80*** |
| SxL | 6.2 | 3 | 0.74ns |
| SxT | 17.9 | 15 | 3.37*** |
| LxT | 2.1 | 5 | 1.18ns*** |
| Error | 45.5 | 16 | |
| SxLxT | 12.9 | 15 | 2.42** |
| Error | 28.3 | 80 | |

[a] Probabilities for significance
***, $P < 0.001$
**, $P < 0.01$
*, $P < 0.05$
ns, not significant

The results of the analysis of variance on conductivity are presented in Table 17 and may be directly related to the results displayed in Figure 28. The sources represented by treatment, time, and treatment-time interaction are significant. This tends to validate the conclusion that fixation affects the conductivity of the leachate and this effect is a function of time. The sources of variance represented by leaching solution-treatment interaction, and solution-time interaction are not significant. These results are similar to those for pH, and demonstrate that leachate quality, as measured by conductivity, is independent of the leaching solution used in this experiment.

Table 17. ANALYSIS OF VARIANCE FOR CONDUCTIVITY: RESIDUE 100

| Source | Sum of squares | Degrees of freedom | F[a] |
|---|---|---|---|
| Residue treatment (S) | $4.87\times10^8$ | 3 | 22.0*** |
| Leaching solution (L) | $9.41\times10^6$ | 1 | 1.28ns |
| Time (T) | $1.97\times10^8$ | 5 | 19.84*** |
| SxL | $8.62\times10^6$ | 3 | 0.39ns |
| SxT | $2.17\times10^8$ | 15 | 7.29*** |
| LxT | $6.38\times10^6$ | 5 | 0.64ns |
| Error | $11.8\times10^7$ | 16 | |
| SxLxT | $1.94\times10^7$ | 15 | 0.65ns |
| Error | $1.59\times10^8$ | 80 | |

[a] Probabilities for significance
***, $P < 0.001$
**, $P < 0.01$
*, $P < 0.05$
ns, not significant

The statistical analysis presented in this section relates to only one residue category and represents a limited sampling. While the results of this analysis support those conclusions previously discussed for residue 100, it is not appropriate at this time to imply that similar analyses would support other conclusions. It is noteworthy that the effect of leaching solution used in this experiment does not significantly affect results for the descriptive parameters. This indicates that the inherent properties of the specimens dominate the chemical properties of leaching. If this relationship holds for the remaining chemical properties, it will significantly reduce the testing required.

Sulfate-The sulfate concentrations in the column leachates are presented by residue category in Figures 38-47, respectively. Sulfate was selected for presentation in this report since it represents a major anionic species present in the residues, particularly the FGD sludges. The data for the raw sludges, except 300 and 700, show high concentrations of sulfate in the leachates (concentrations which exceed those desirable for normal water quality). In these cases the sulfate concentrations are stable with respect to time or demonstrate a decrease. This fact is possibly coupled to the solubilities of the sulfate compounds existing in the residues, the more soluble forms being leached at a high, rapid rate, and the less soluble forms being limited by solubility to a relatively stable leach rate. Those residues reflecting the former condition include 800 and 1000, and those reflecting the latter include 100, 200, 400, 500, 600, and 900. Both 800 and 1000, Figures 45 and 47, are characterized by fairly stable leach rates for sulfate after a high initial leach rate. This is presumably related to transition from a soluble sulfate form, which is readily leached, to a form which is leached at a solubility limited rate. The plots for residues 300 and 700, Figures 40 and 44, are highly variable and do not exhibit any trends which appear to be significant.

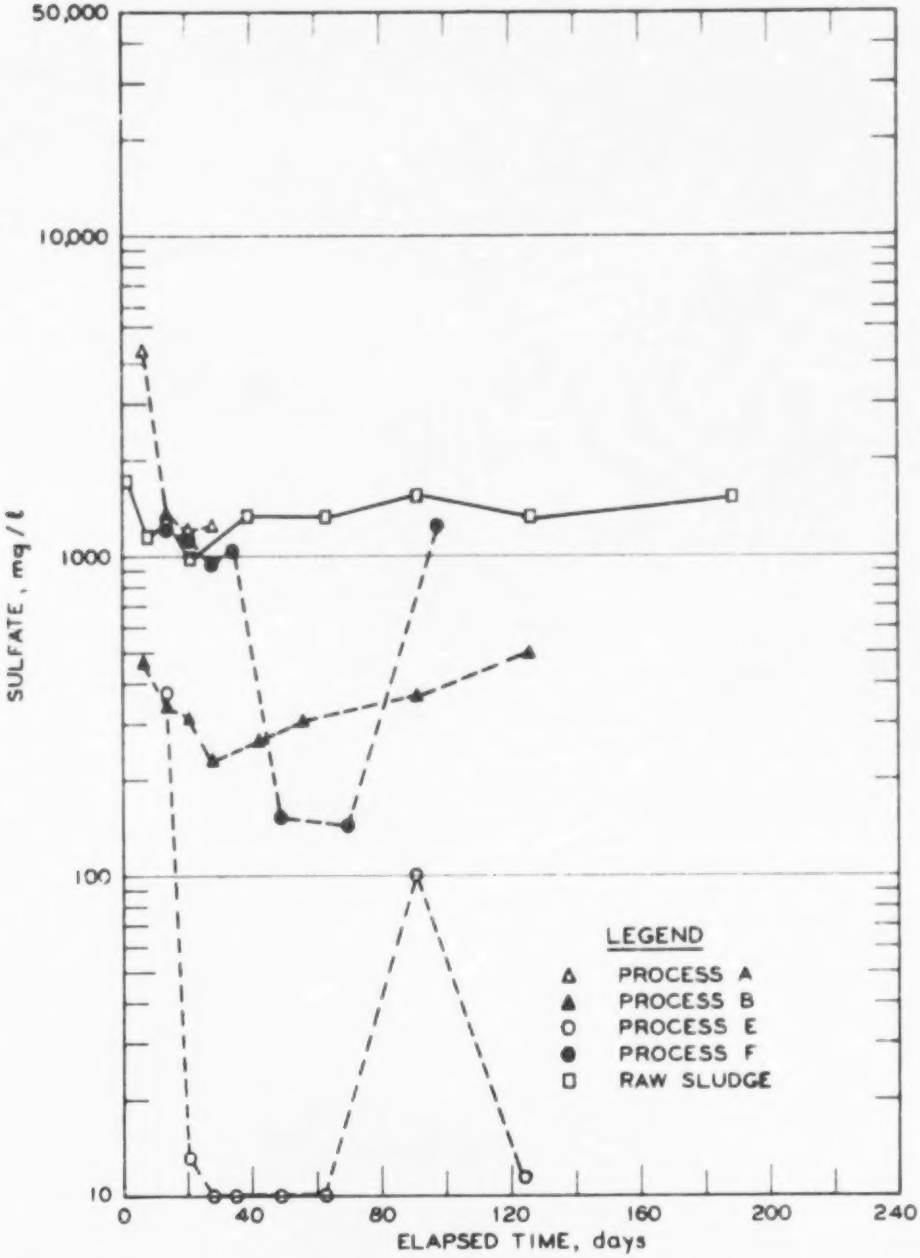


Figure 38. Sulfate concentration versus time, raw and fixed residues: Number 100.

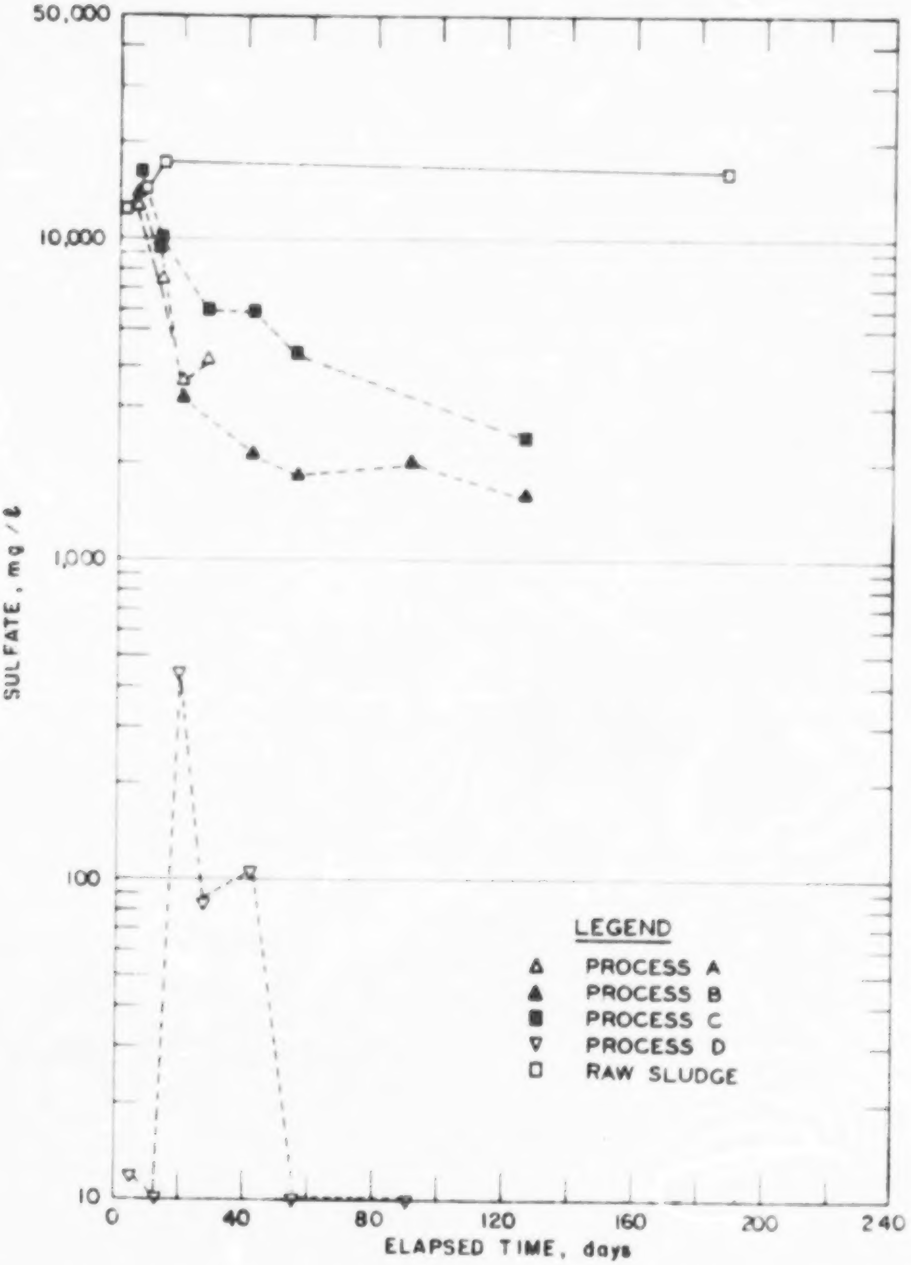


Figure 39. Sulfate concentration versus time, raw and fixed residues: Number 200.

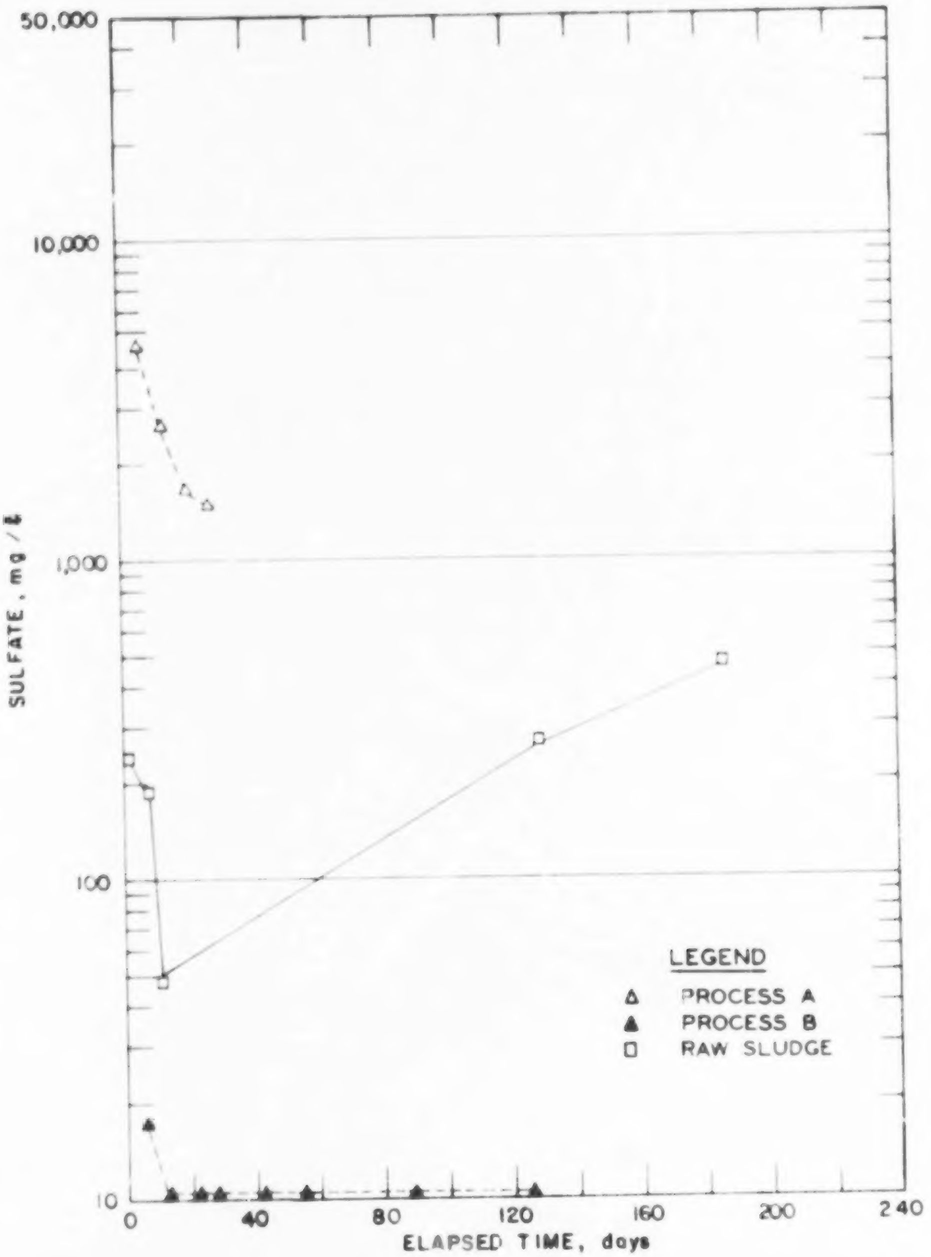


Figure 40. Sulfate concentration versus time, raw and fixed residues: Number 300.

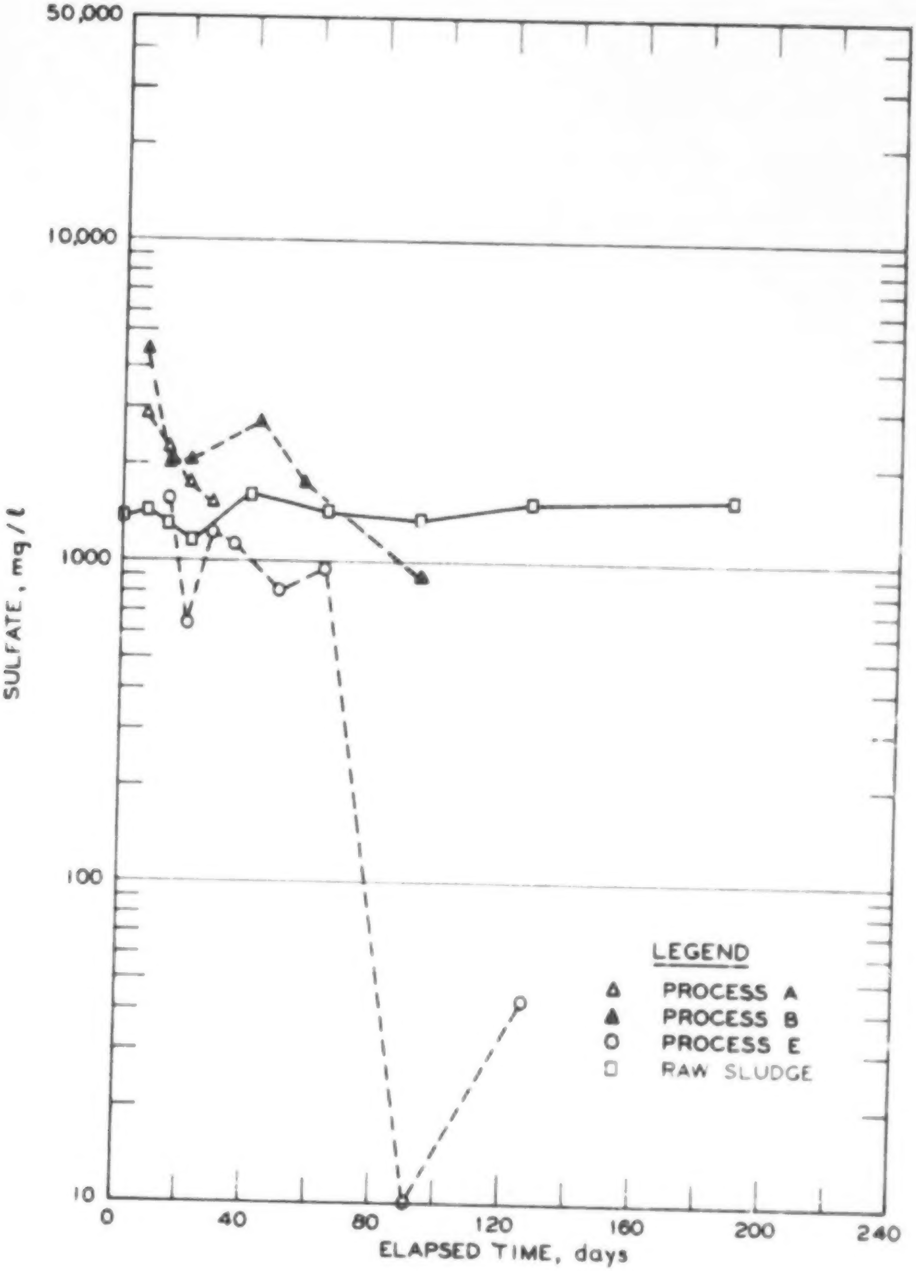


Figure 41. Sulfate concentration versus time, raw and fixed residues: Number 400.

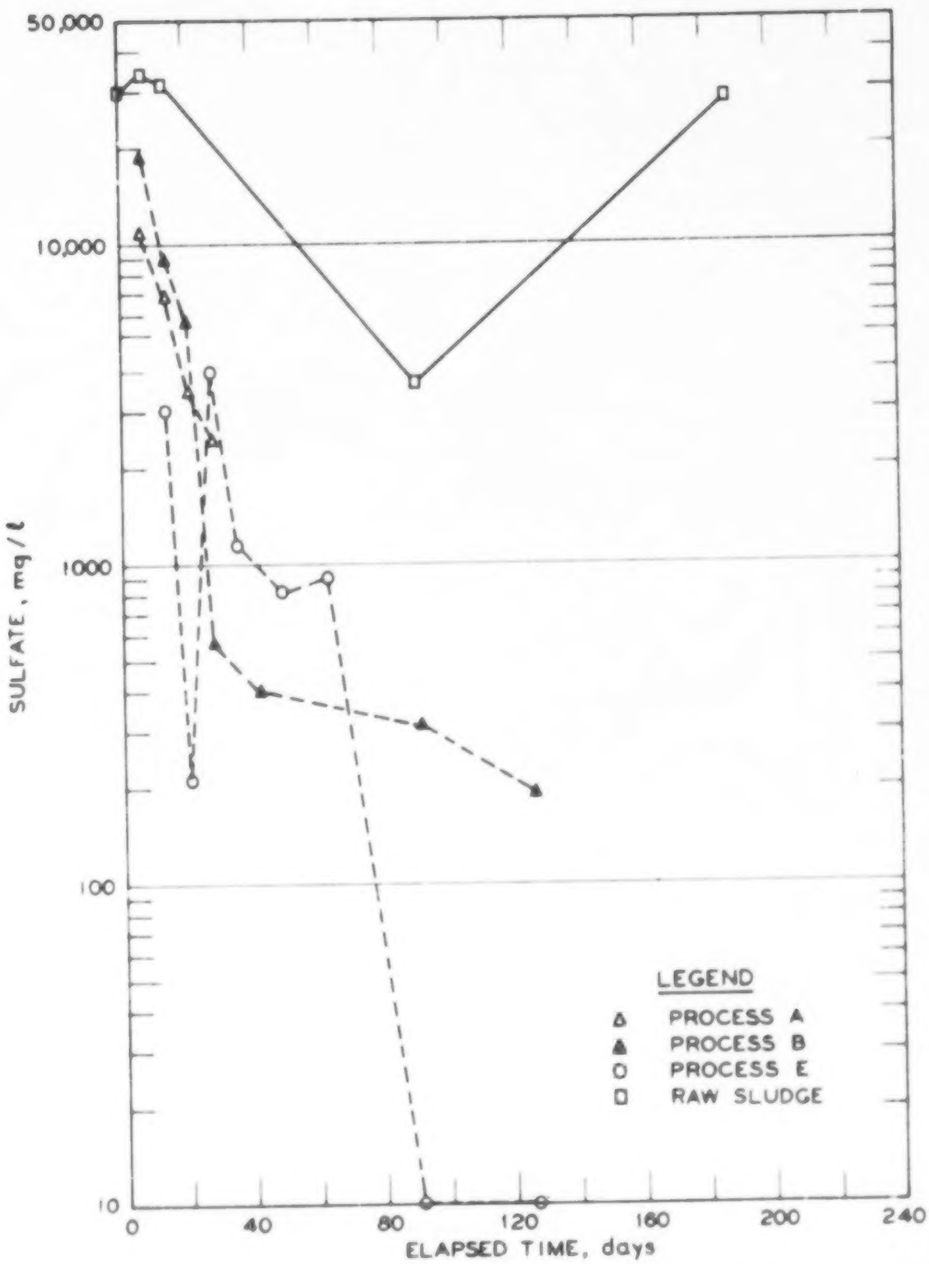


Figure 42. Sulfate concentration versus time, raw and fixed residues: Number 500.

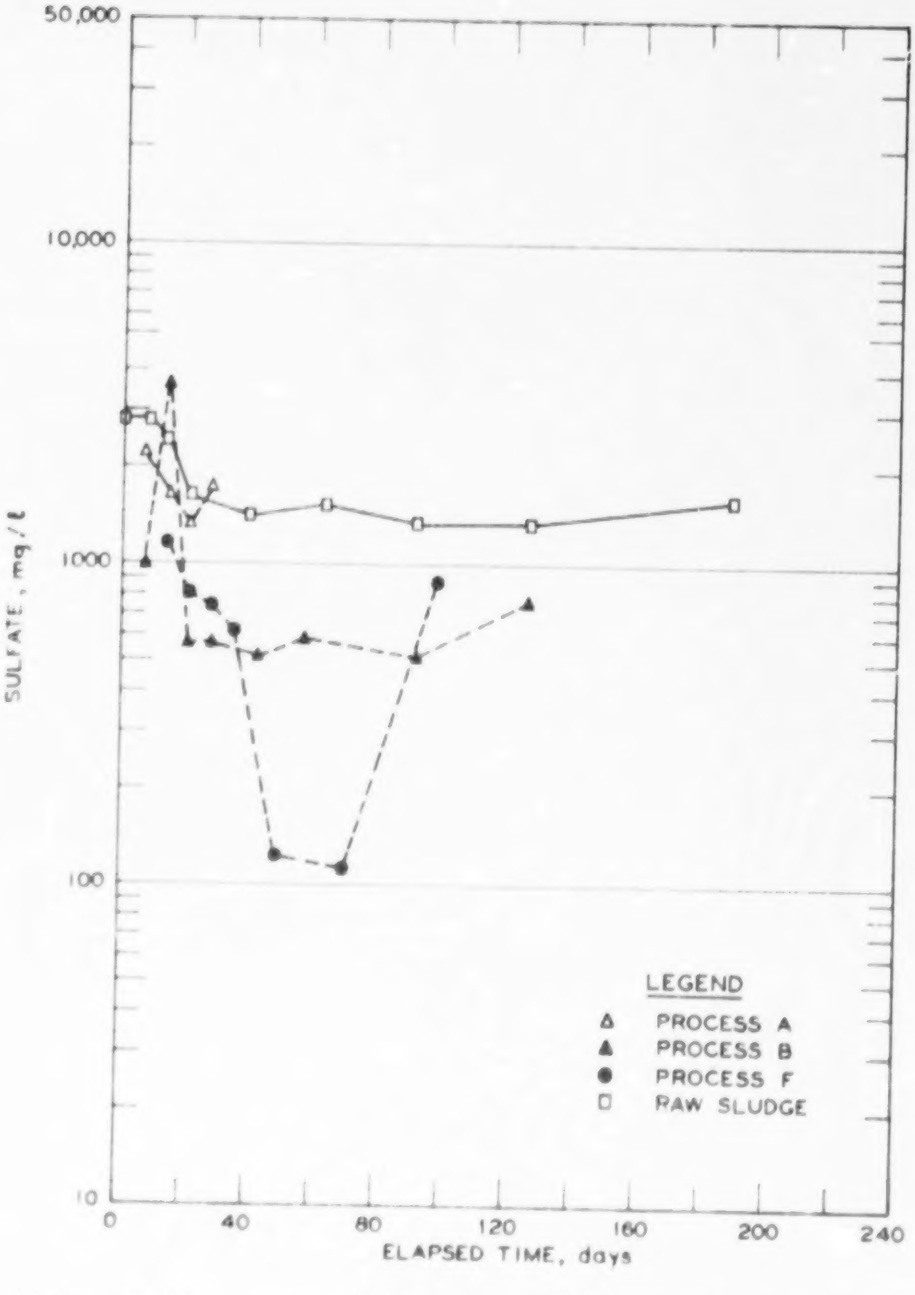


Figure 43. Sulfate concentration versus time, raw and fixed residues:
Number 600.

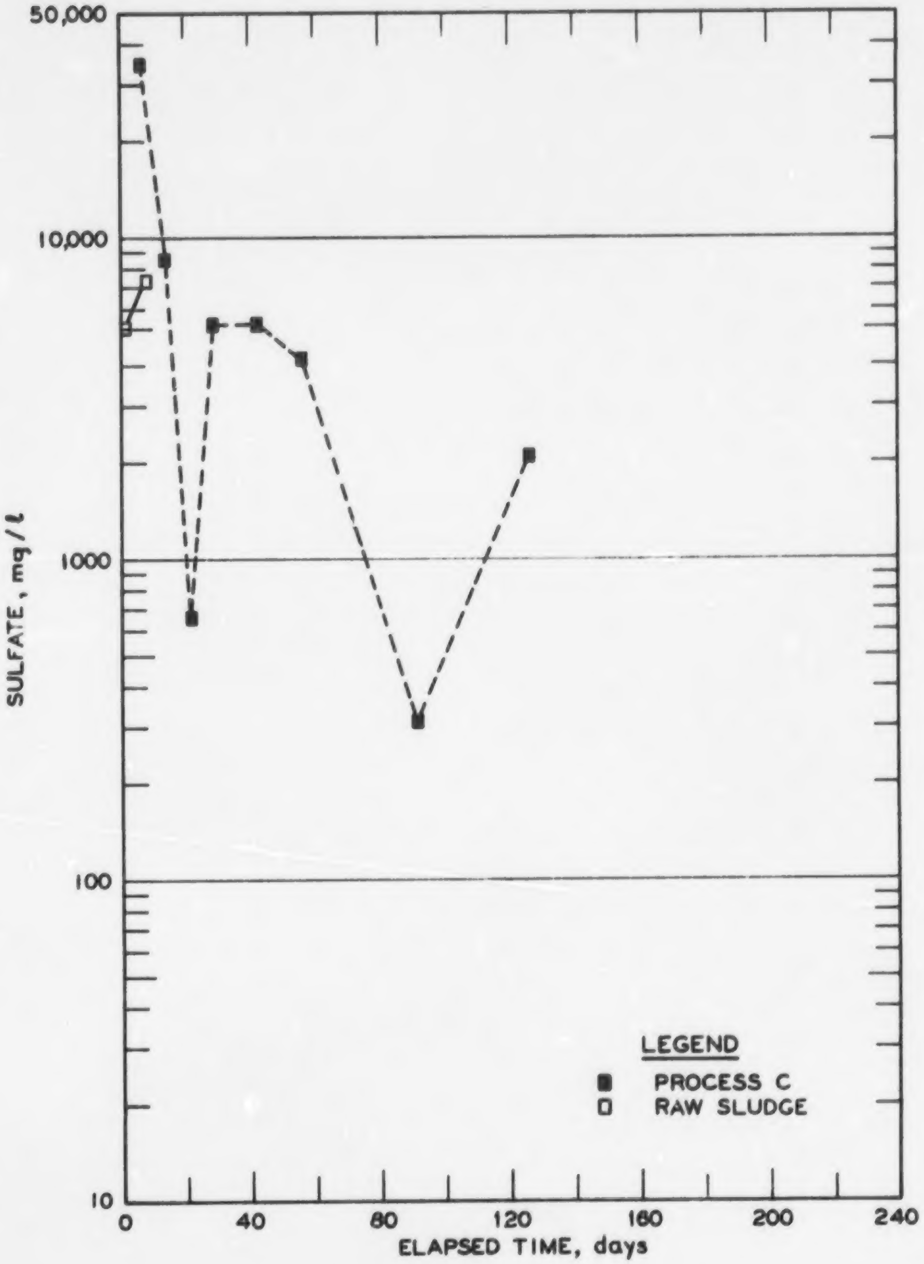


Figure 44. Sulfate concentration versus time, raw and fixed residues: Number 700.

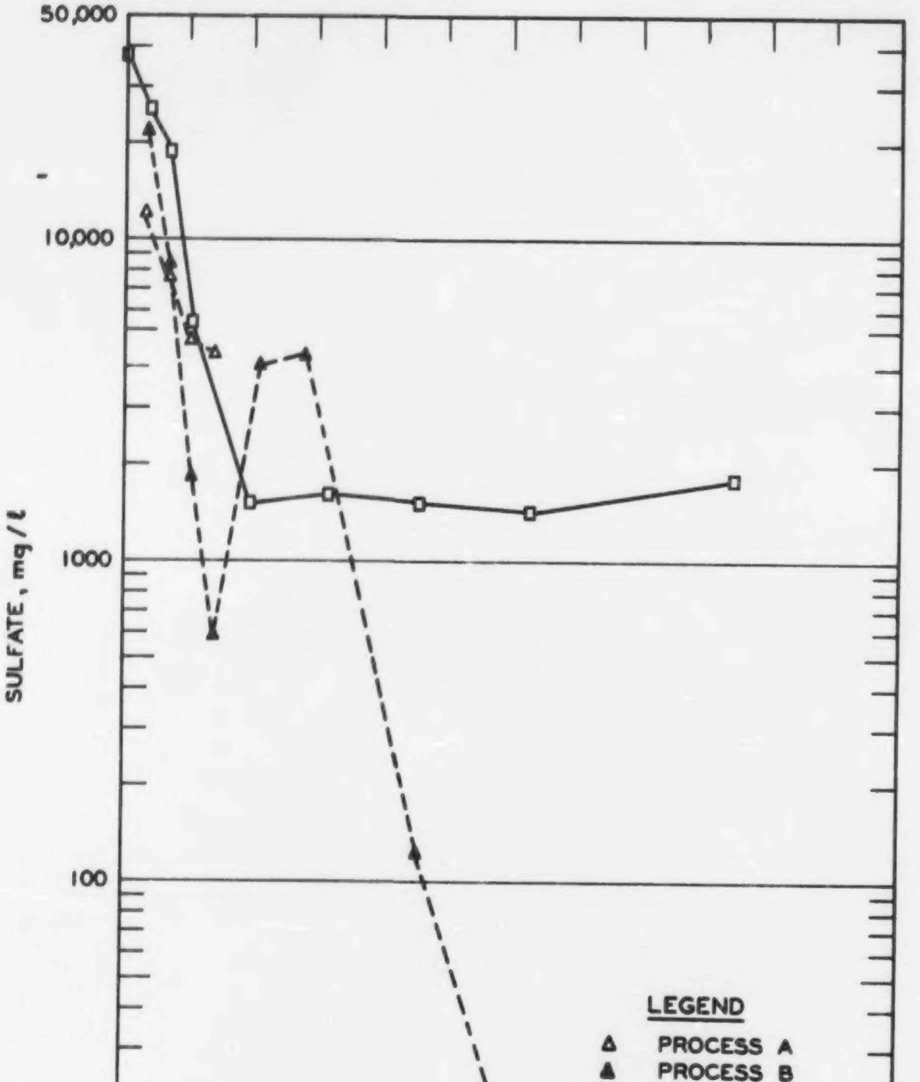


Figure 45. Sulfate concentration versus time, raw and fixed residues: Number 800.

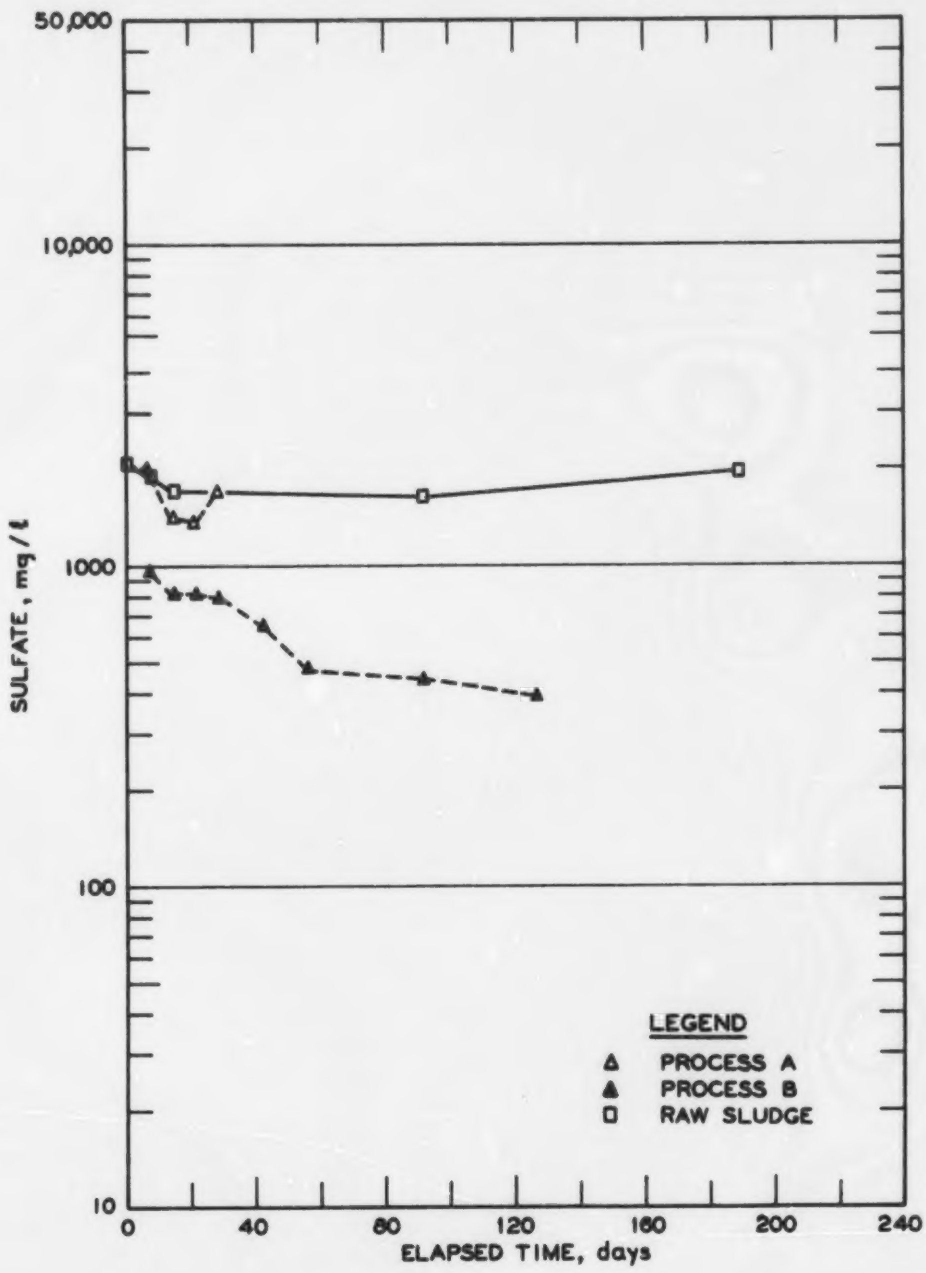


Figure 46. Sulfate concentration versus time, raw and fixed residues: Number 900.

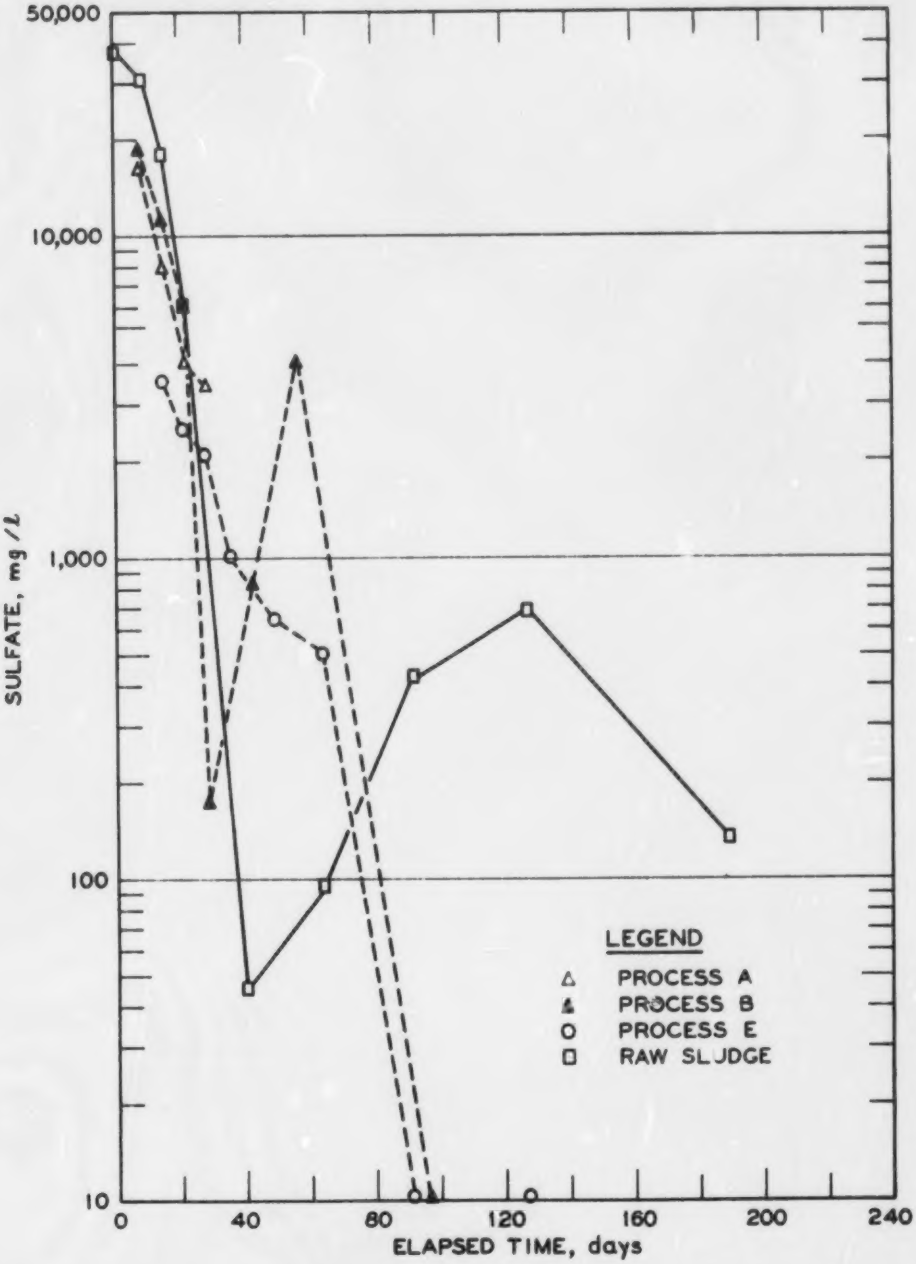


Figure 47. Sulfate concentration versus time, raw and fixed residues: Number 1000.

Examination of Figures 38-47 demonstrates that fixation seems to be effective in retarding sulfate mobility from the residues. The retardation is in relationship to the sulfate mobility exhibited by the raw sludges. Most of the fixed specimens were characterized by sulfate leaching, in many cases at high concentrations, at a rapidly decreasing rate (e.g., Figure 42). This behavior indicates that very soluble forms of sulfate are not retained by fixation, and are initially leached from the fixed residues.

Some of the sulfate leach data for fixed residues, Figures 38, 39, 41, and 43, demonstrate a decline in sulfate concentration in the leachate initially but appear to be increasing at the latter stages of leaching. This observation cannot be confirmed since there is not sufficient data at present to reestablish a trend. If a trend is established, it may be related to a shift in equilibrium resulting in increased sulfate availability. A possible shift in equilibrium has been noted earlier with respect to the temporal pH shift.

*Copper*-Copper data are presented in this report as an example of the leachate behavior for a metal. The results for copper are presented by residue category in Figures 48-57, respectively. Reported values are the means of all replicates. Except for low level (< 20 ppb) data for the raw residues the leaching of copper is stable or data well behaved for all residues. Well-behaved leaching is defined by a decreasing concentration versus eluted volume. In some cases the data are variable for raw sludges, Figure 52, but there is insufficient data for this case to determine a probable trend. The suggested water quality limit for copper is 1.0 mg/ℓ[20] and only one raw residue, Figure 49, demonstrated a leachate that exceeds this standard in a consistent manner.

The leachate behavior for the fixed residues exhibited three definite patterns. All fixation processes demonstrated leaching of copper in some manner. For some of the residue categories the fixed specimens possessed well-behaved leaching characteristics and the concentration of copper decreased to low levels rapidly. A low level of copper would be approximately 10 ppb, which is below the detection limit of conventional flame atomic absorption, and is probably not environmentally significant since copper is a required micronutrient. Furthermore, levels of copper below 10 ppb are probably not significantly different from blank columns, Table 15. In the case of residues 100, 400, 700, and 800, the leaching of copper is equivalent to, or slightly greater than the raw sludges, but appears to be increasing with time. This fact again alludes to the apparent pH shift which is occurring for fixed residues with respect to time. In the case of residue 200, an interesting observation may be made regarding the different types of fixation processes. Process B is performing roughly equivalent to the raw sludge, process D in a superior fashion, and process C in a fashion worse than the raw sludge. This divergence in process behavior for a particular residue demonstrates the effect of fixation processing on leaching properties of a product.

To present a more complete understanding of the leaching behavior for copper, the data for residue 200 are presented as mass leach rates.[4] The mass leach rates were evaluated by use of the following equations:

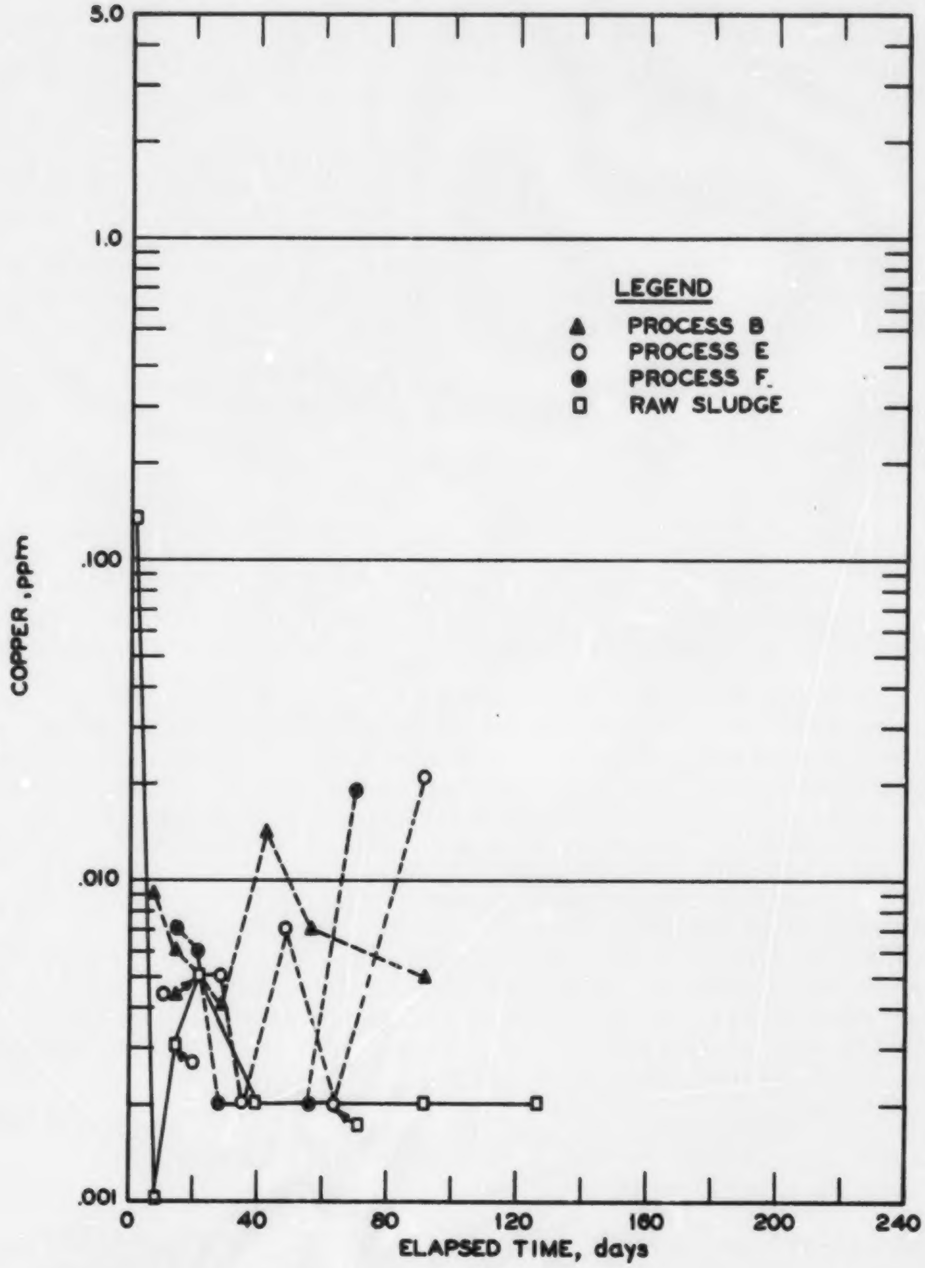


Figure 48. Copper concentration versus time, raw and fixed residues: Number 100.

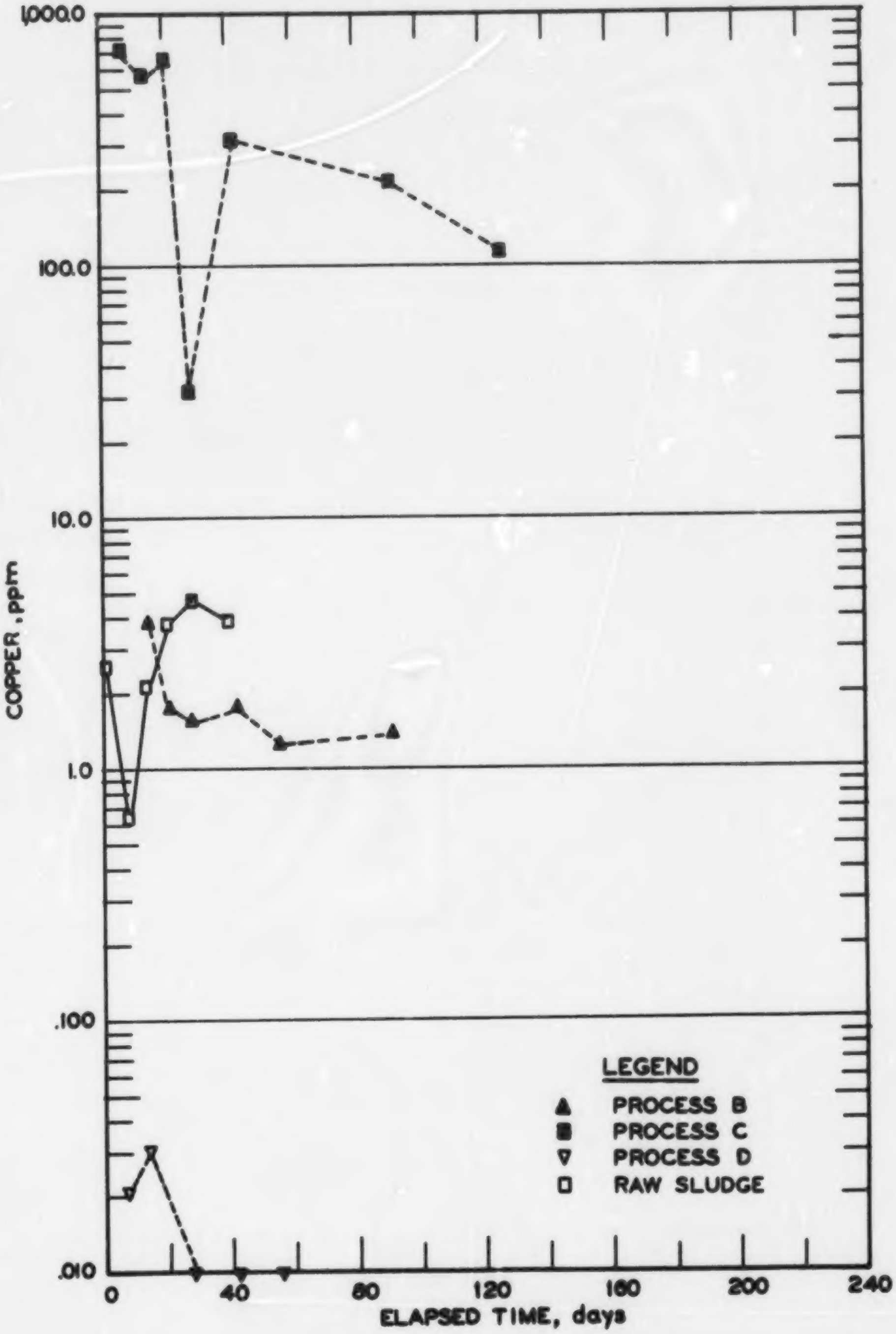


Figure 49. Copper concentration versus time, raw and fixed residues: Number 200.

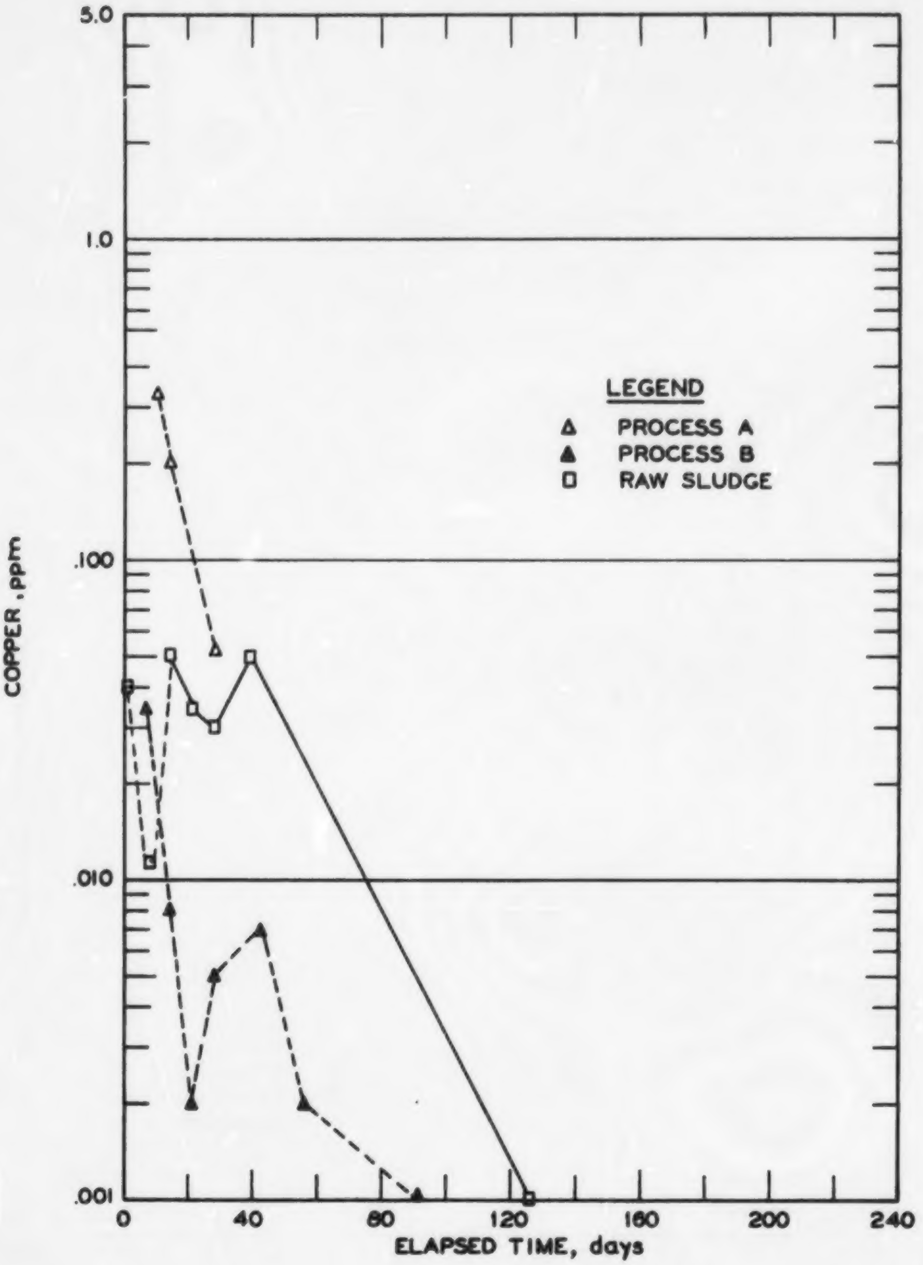


Figure 50. Copper concentration versus time, raw and fixed residues: Number 300.

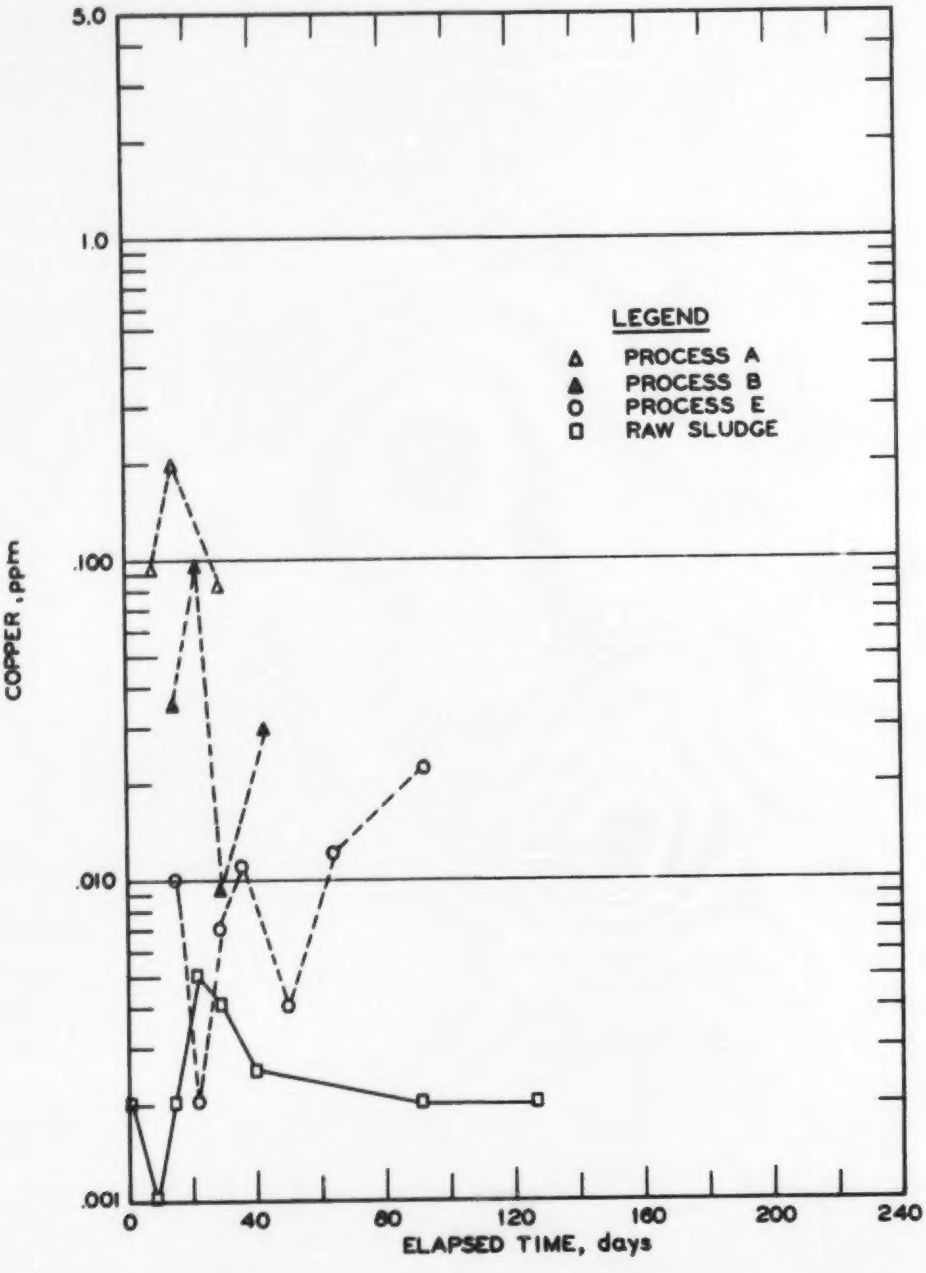


Figure 51. Copper concentration versus time, raw and fixed residues: Number 400.

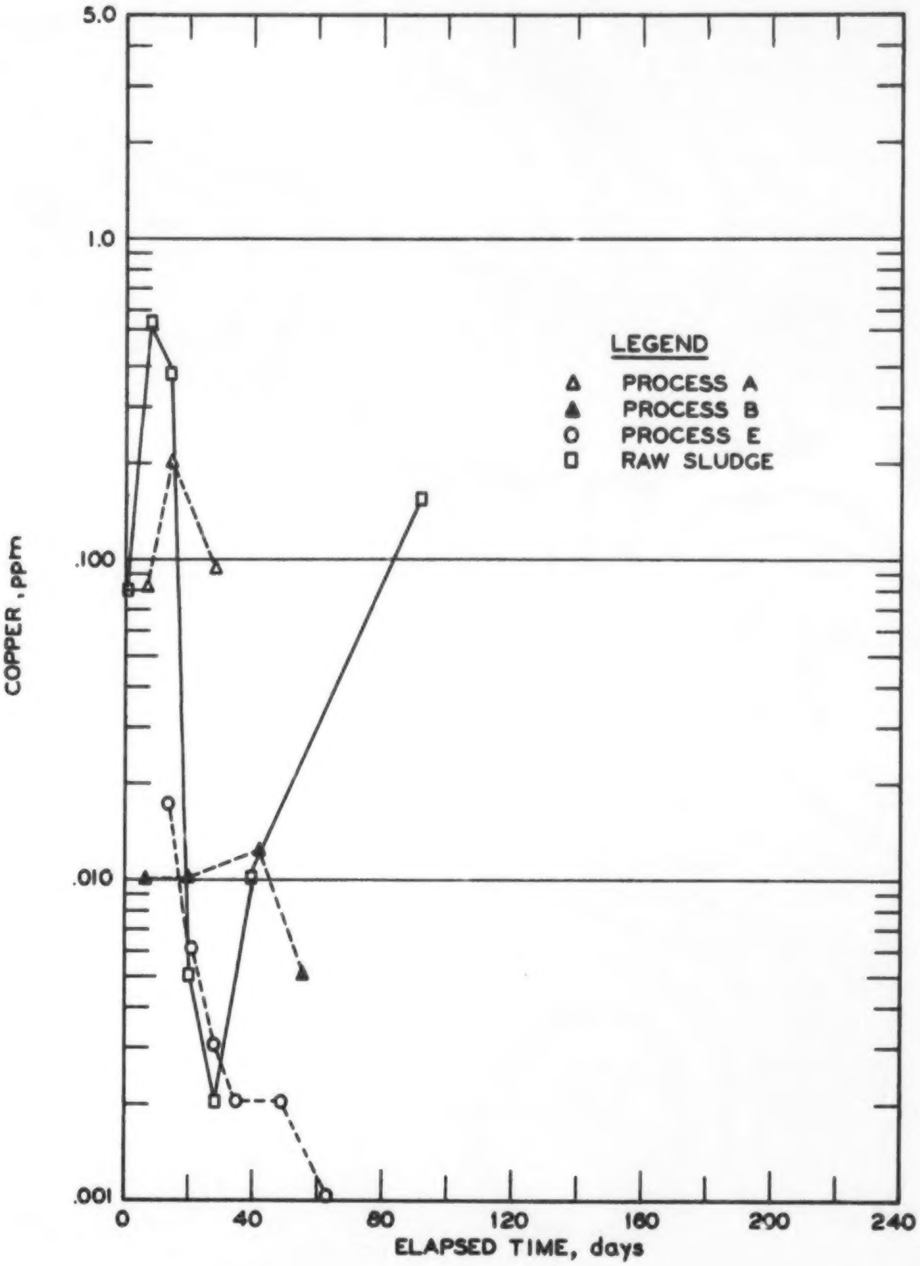


Figure 52. Copper concentration versus time, raw and fixed residues: Number 500.

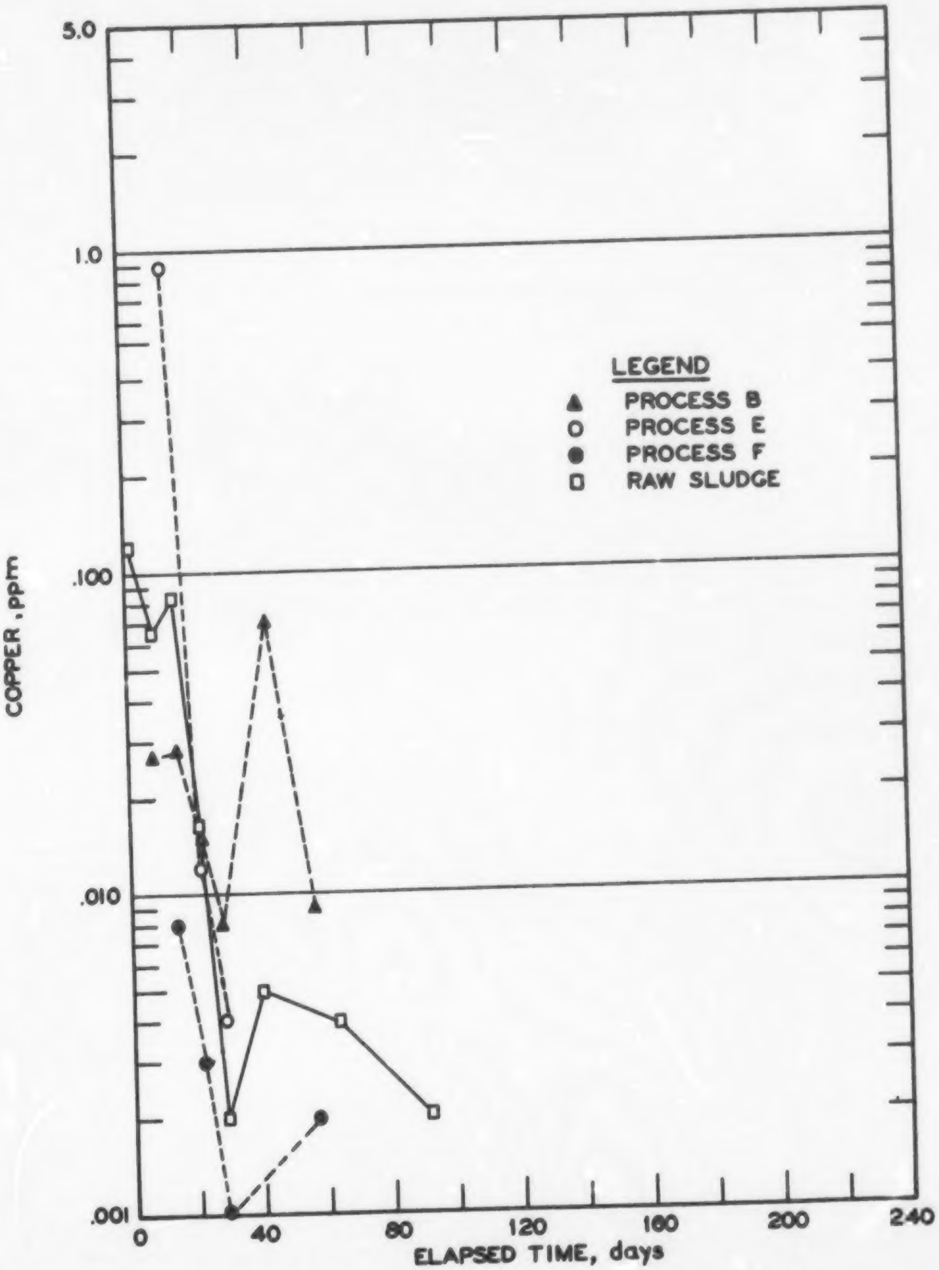


Figure 53. Copper concentration versus time, raw and fixed residues: Number 600.

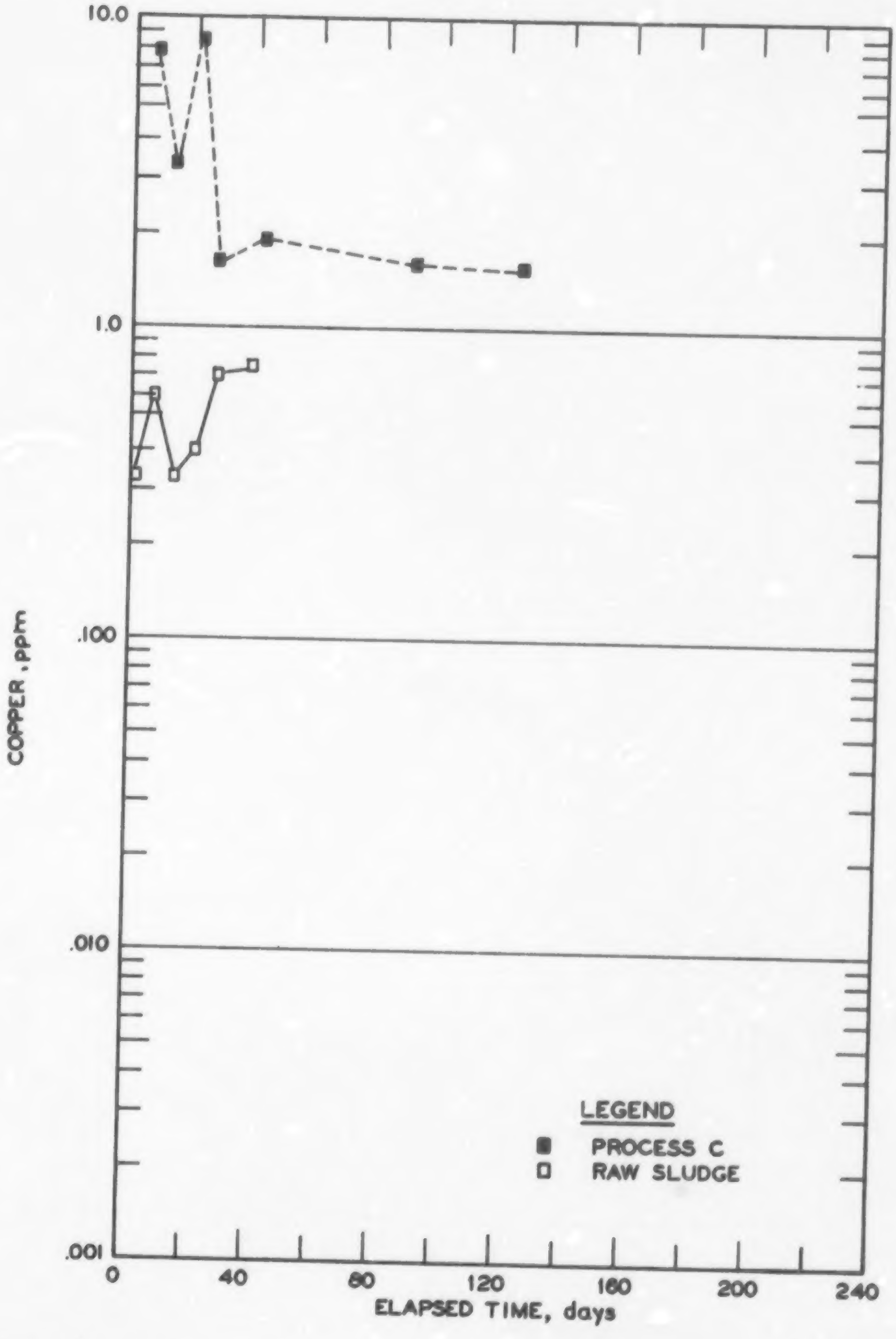


Figure 54. Copper concentration versus time, raw and fixed residues: Number 700.

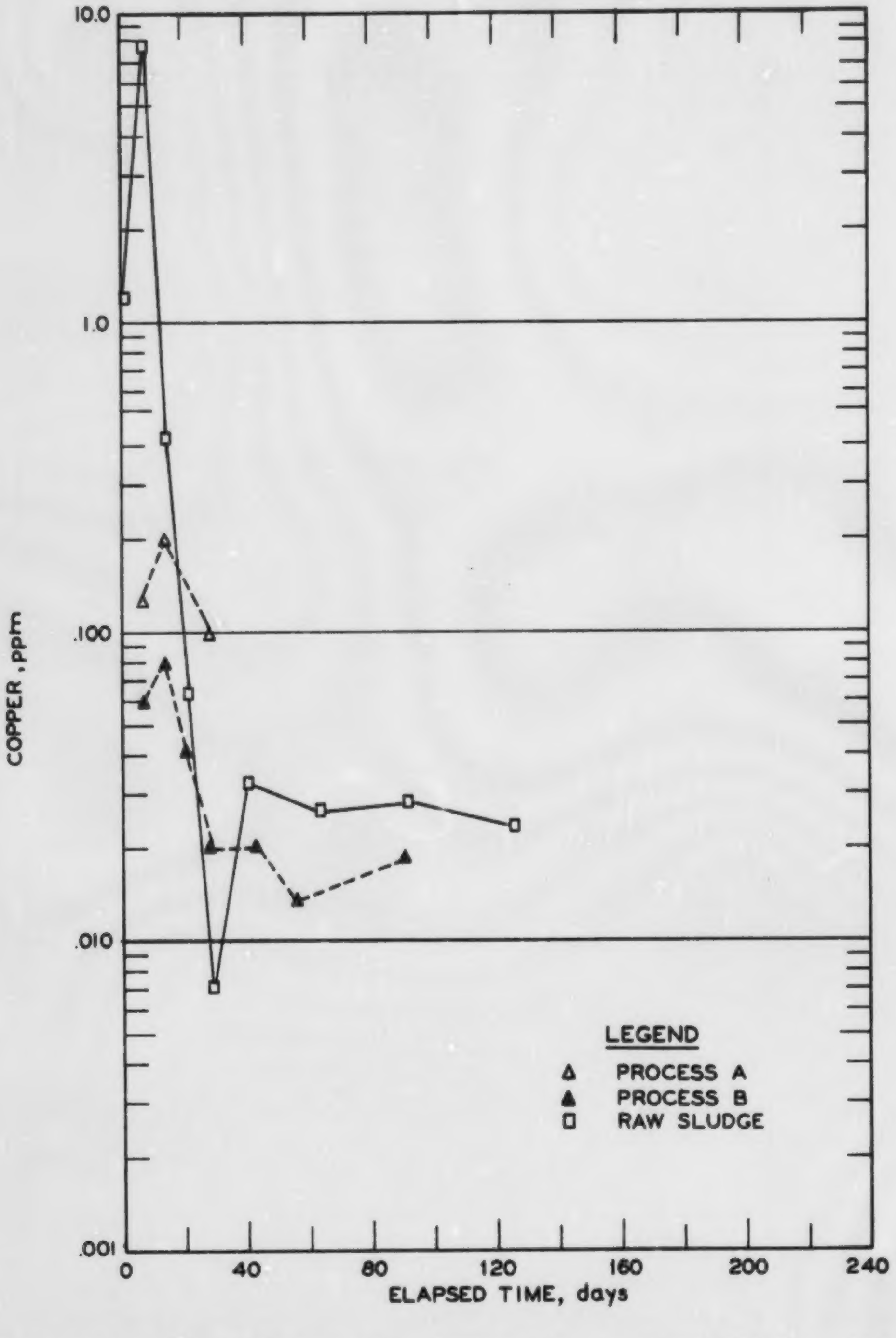


Figure 55. Copper concentration versus time, raw and fixed residues: Number 800.

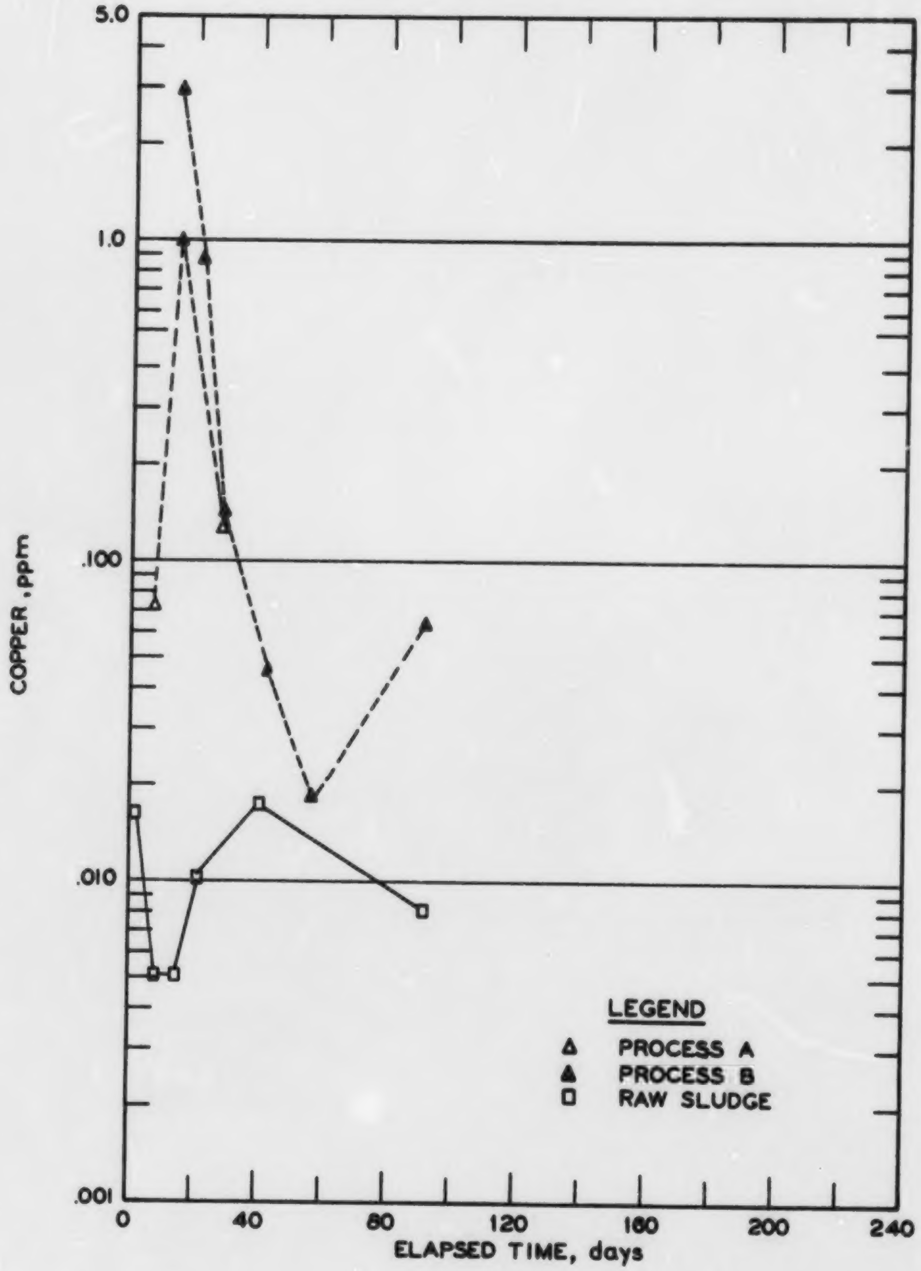


Figure 56. Copper concentration versus time, raw and fixed residues: Number 900.

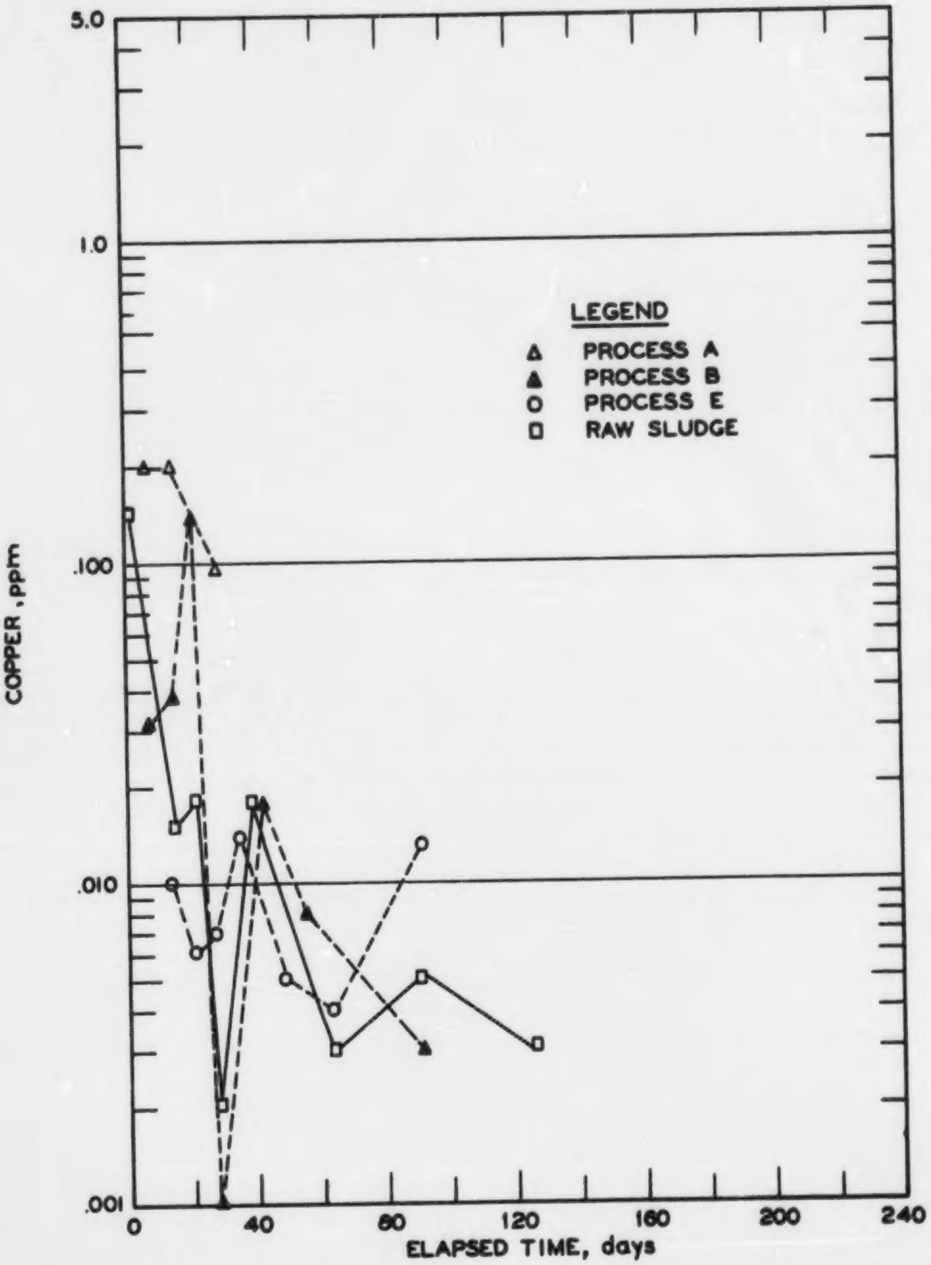


Figure 57. Copper concentration versus time, raw and fixed residues: Number 1000.

(a) $\frac{\Sigma a_n}{A_o} \cdot \frac{V}{s}$ versus $\Sigma t_n$

(b) $\frac{\Sigma a_n}{A_o}$ versus $(\Sigma t_n)^{1/2}$

(c) $\frac{a_n}{A_o} \cdot \frac{V}{s} \cdot \frac{1}{t_n}$ versus $(t - t_n/2)$

Where:
$a_n$ = Species mass lost during leaching period, (mg)
$\Sigma a_n$ = Sum of all $a_n$
$A_o$ = Initial species mass in column, (mg)
$V$ = Volume of specimen, ($cm^3$)
$S$ = Exposed surface area, ($cm^2$)
$t_n$ = Duration of leachant renewal period
$\Sigma t_n$ = Sum of $t_n$

The first two equations, (a) and (b), present the data as cumulative amounts of any species lost for a leaching period. In this fashion, the total amount of any particular species lost for a leaching period may be determined graphically. The third method (c), presents results for each leaching period separately; therefore, it has the advantage of not being dependent on past analysis, eliminating any cumulative bias due to experimental errors. Note that methods (a) and (c) include the volume to surface area ratio in the presentation of results. This technique assumes that the surface area to volume ratio is one of the controlling factors for leaching and also allows comparison of results among columns using different fixation techniques. In this manner, the success of the applied fixation techniques may be compared graphically. Volume to surface area ratios were approximated from sample geometry and the additives of fixation were assumed to add no copper to the residue (mass dilution).

Cumulative leach rates are plotted against time and the square root of time in Figures 58-59 and 60, respectively. Figures 58-59 include the exposed volume to surface area term within the cumulative fraction leached. Comparison between the leaching properties of the raw and fixed sludges may be made from these plots, but some caution must be exercised in doing so. The effect of the volume to surface area ratio for the plots will be pronounced when comparing data from the raw sludges against the fixed. The plots of cumulative leach rates for method (a), Figures 58-59, demonstrate that leaching is approaching an equilibrium point, as characterized by the tendency to approach constant values for fraction cumulatively leached. The plots of cumulative leach rates for method (b), Figure 60, have the advantage of

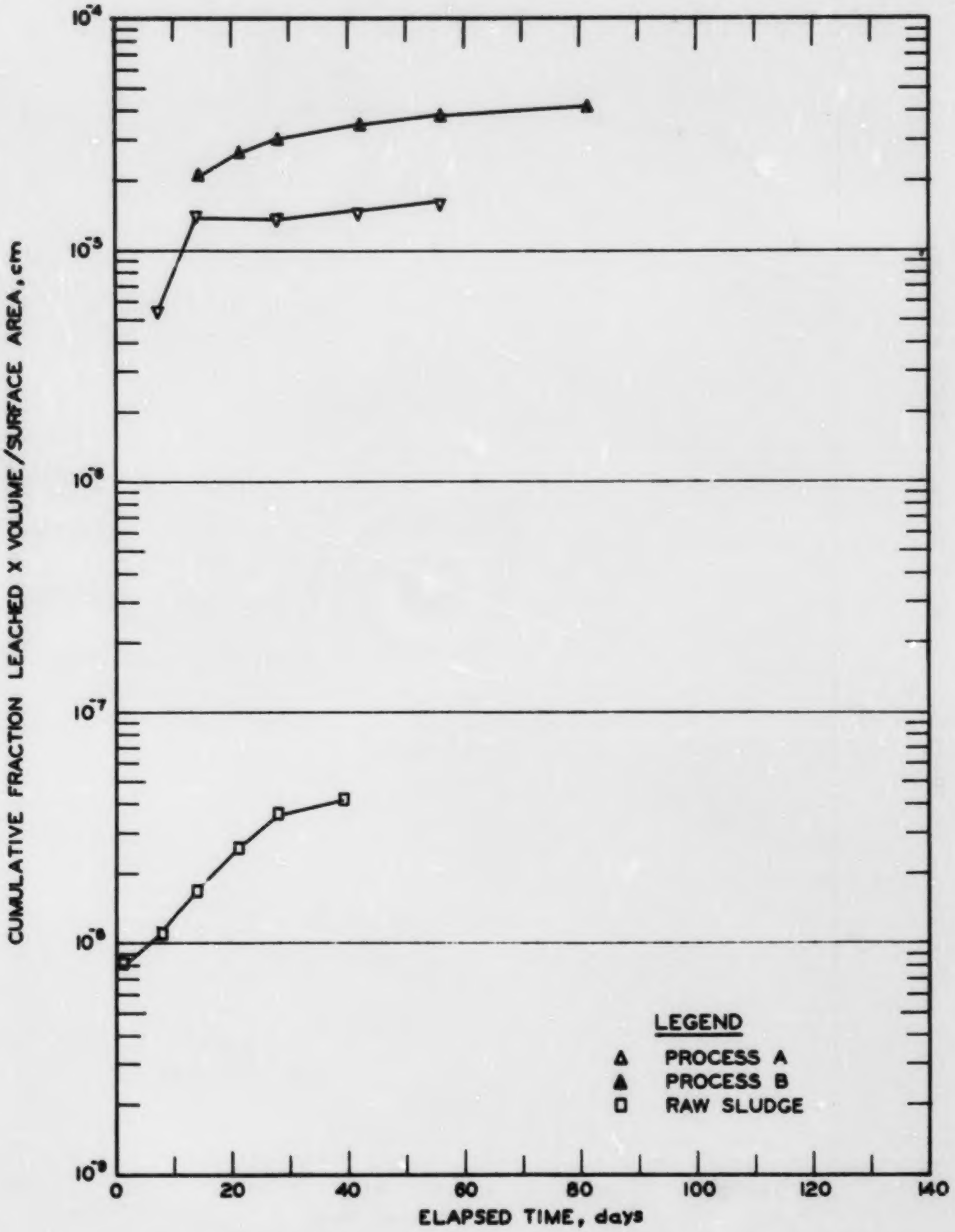


Figure 58. Cumulative leaching, rate, copper: Residue 200 (c) versus time (R,A,B).

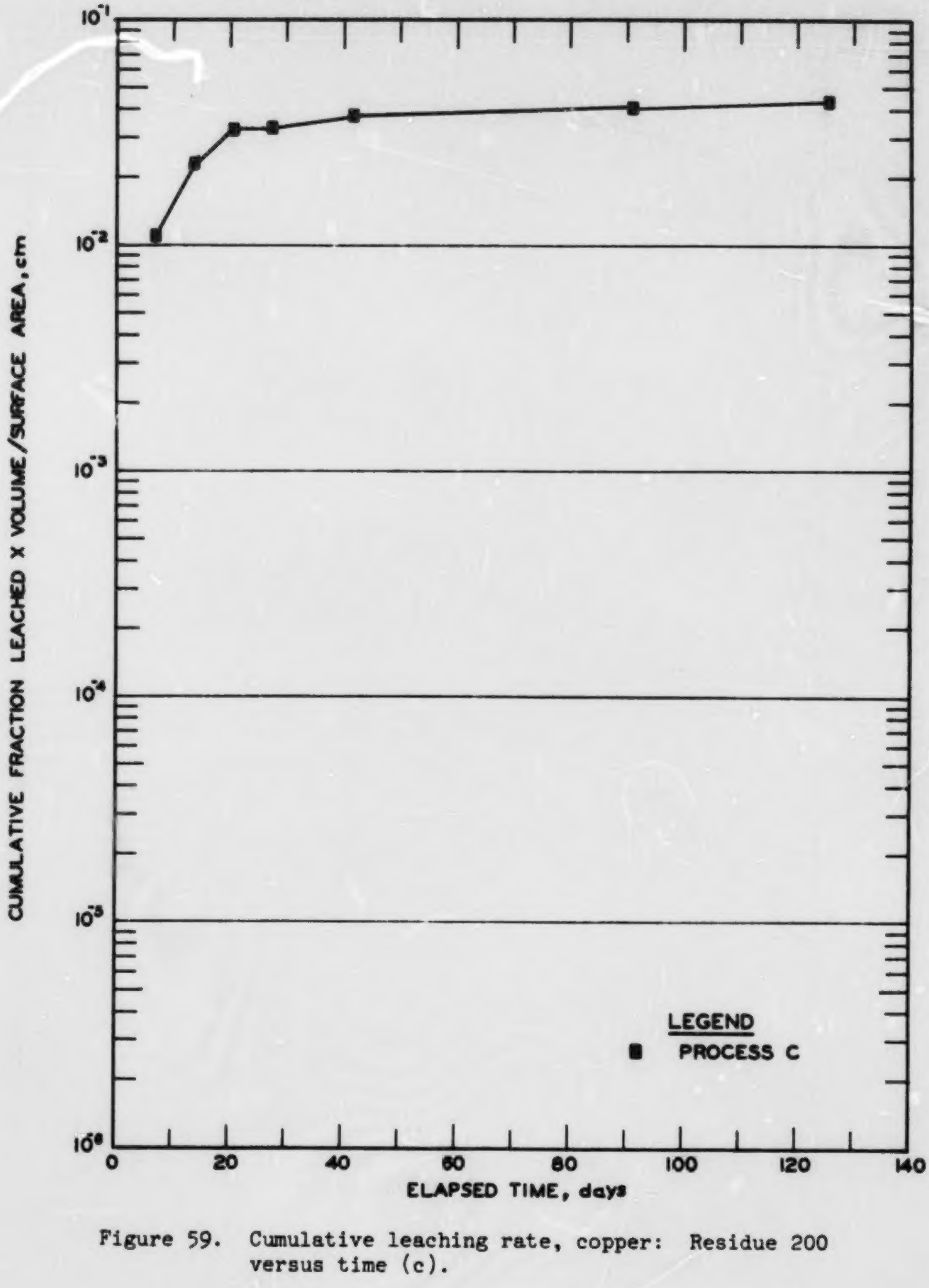


Figure 59. Cumulative leaching rate, copper: Residue 200 versus time (c).

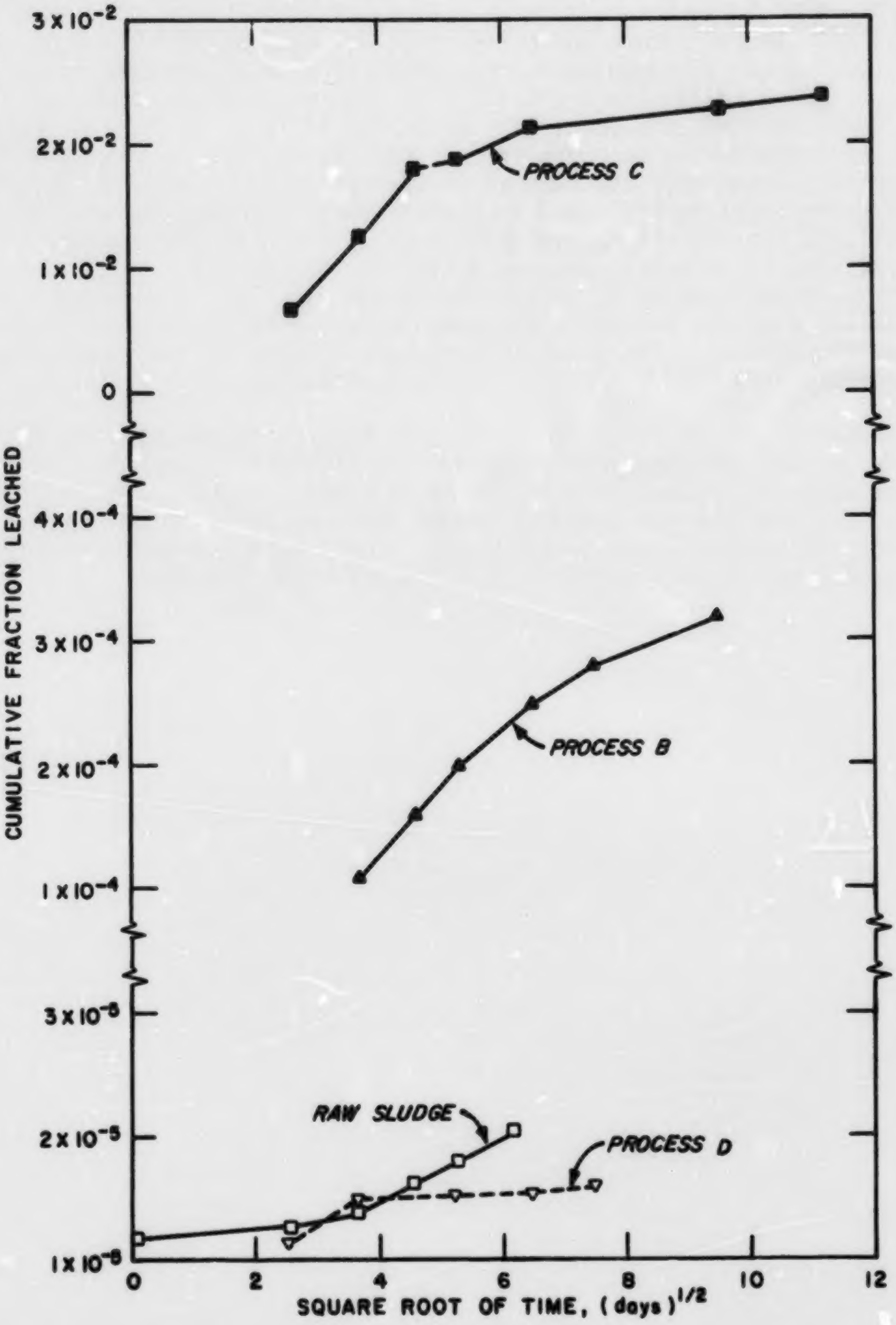


Figure 60. Cumulative leaching rate, copper: Residue 200 versus square root of time.

assuming a linear form. The assumption of a linear form permits calculation of an "apparent" leach rate from the slopes of these plots. The results of this calculation result in an ordering for leaching of D < R < B < C. This ordering may be compared to that obtained from the concentration data, Figure 49 which results in D < B < R < C. In making this comparison, it should be noted that the total mass of pollutant (e.g. copper) present in the leached samples is much greater for the raw sludges than for the fixed specimens; consequently the cumulative fraction leached would be expected to be low in relation to the fixed specimens. These observations are not consistent with the ordering presented for pH (C < D < R < B) demonstrating the effect of sample geometry upon evaluation of leaching data. This inconsistency may, in the case of D, be related to the fact that D is an encapsulation process and does not behave in the same manner as the other processes with respect to leaching. The point of agreement between pH and copper leaching may be related to the pH effect discussed previously.

The incremental leach rates are plotted in Figures 61 and 62. These data include the elapsed time between column sampling periods and consequently are not subject to cumulative errors as were the previous plots, Figures 58-60. The data for all residues, fixed and raw, are reasonably well behaved. These plots also indicate that leaching is approaching a stable state and demonstrate the effect of surface area alteration.

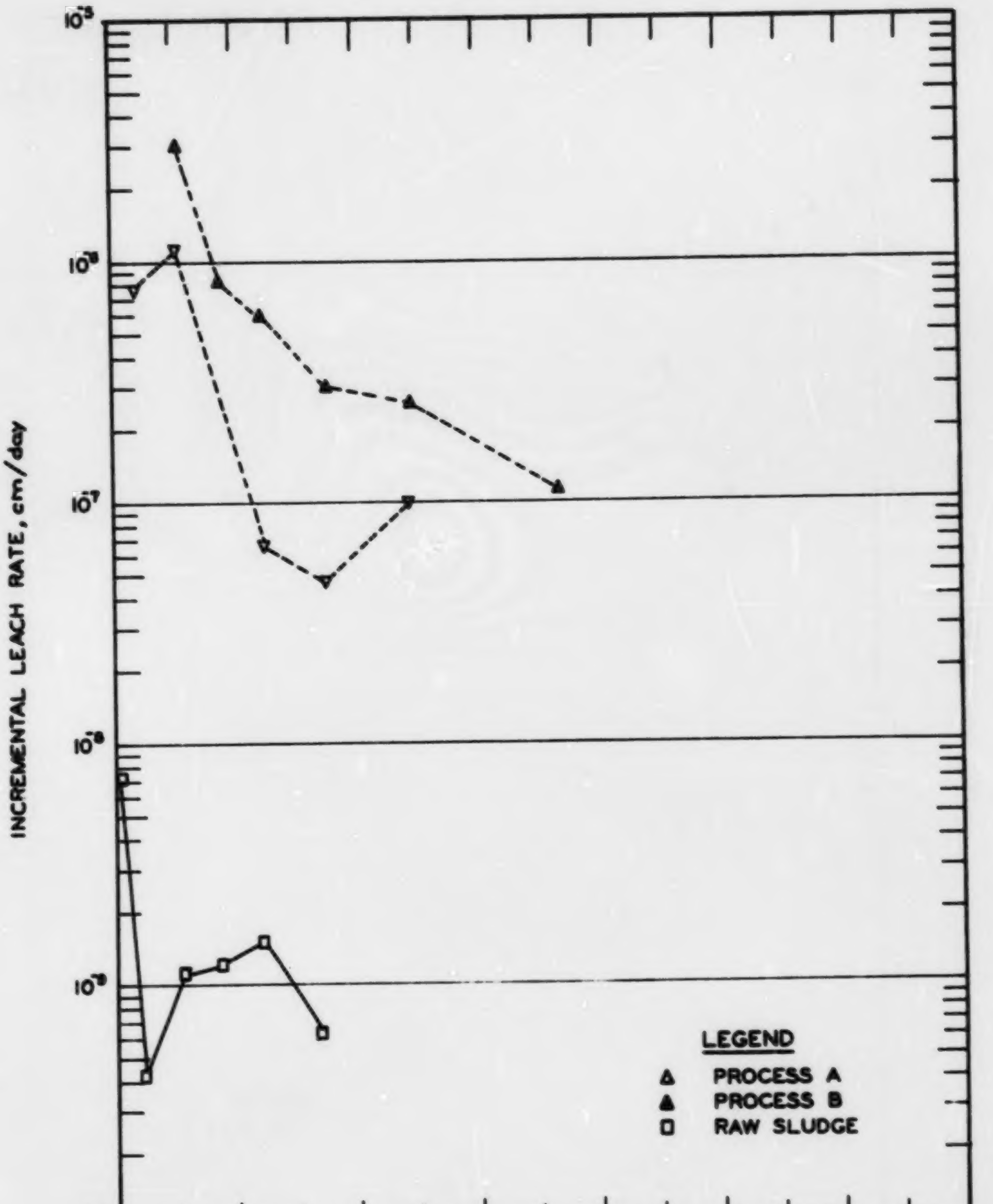


Figure 61. Incremental leaching rate, copper: Residue 200 (R,A,B).

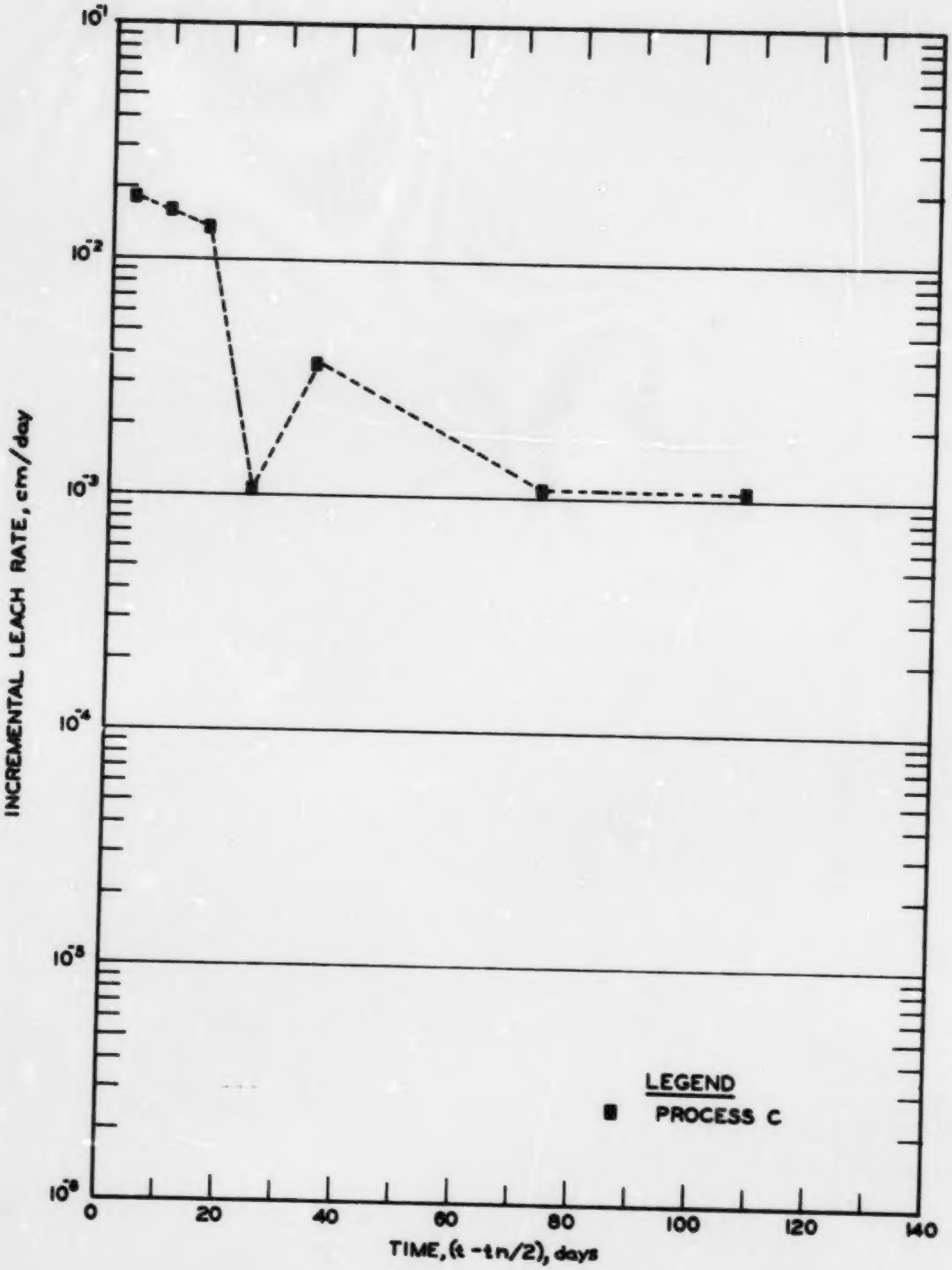


Figure 62. Incremental leaching rate, copper: Residue 200 (c).

## SECTION VII

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